THE UNIVERSITY OF ALBERTA

Vapor Pressures of Ammonia and Carbon Dioxide in Equilibrium with Aqueous Solutions of Monoethanolamine

Faculty of Engineering

Department of Chemical and Petroleum Engineering

by

Abdul Rahman

Edmonton, Alberta.

September, 1959.

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THE UNIVERSITY OF ALBERTA

VAPOR PRESSURES OF AMMONIA AND CARBON DIOXIDE IN EQUILIBRIUM WITH AQUEOUS SOLUTIONS OF MONOETHANOLAMINE

A Dissertation
submitted to
The Faculty of Graduate Studies
in Partial Fulfilment
of the Requirements for the Degree
of Master of Science in Chemical Engineering

Department of Chemical and Petroleum Engineering

by

Abdul Rahman

Edmonton, Alberta

September, 1959

ABSTRACT

The principal object of this investigation was to determine the mutual influence of ammonia and carbon dioxide on their absorptions in the aqueous solutions of monoethanolamine.

The investigation was carried out with 1.0 N, 5.0 N and 9.0 N monoethanolamine solutions at atmospheric pressure and temperatures 70°, 80° and 90°. The experimental procedure consisted of first introducing a known amount of the monoethanolamine solution into the equilibrium cell and then adding measured volumes of ammonia and carbon dioxide. The equilibrium was obtained by vigorous shaking of the equilibrium cell. The vapor phase analysis of ammonia and carbon dioxide was done by absorbing these gases in 0.1 N H_2SO_4 and 0.1 N NaOH respectively.

The experimental results indicated that the partition factor of ammonia increases with the rise of ratio $CO_2:NH_3$ in solution and also with the increase of the normality of monoethanolamine. The ratio $CO_2:NH_3$ in solution has a significant influence on partial pressures of ammonia and carbon dioxide whereas normality of monoethanolamine solutions does not have any significant effect.

ACKNOWLEDGMENTS

The author is particularly indebted to Dr. D. B. Robinson, under whose supervision this project was carried out, and whose guidance, criticism and patience has contributed greatly to this investigation.

The assistance offered by Mr. R. Kirby and Mr. F. Butz, with the construction of the apparatus is very much appreciated.

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[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

LIST OF SYMBOLS

K	Partition Factor, moles of component per 1000 gram of water in solution - divided by moles of component per litre of gas.
n	Number of Moles of a Component in the Gas Phase
P	Total Pressure (Absolute), mm Hg
p	Partial Pressure, mm Hg
R	Universal Gas Constant
T	Absolute Temperature, °K
V	Volume in Gas Phase, litres
X	Molality of a Component in Solution
x	Mole Fraction of a Component in Liquid Phase
y	Mole Fraction of a Component in Vapor Phase

I. INTRODUCTION

Mixtures of carbon dioxide and ammonia with or without other fixed gases and water vapor are encountered in many industrial processes. Thus for example such mixtures are found in coal gas, coke oven gas and in the synthesis of urea. Aqueous solutions of sodium and potassium hydroxide, bicarbonates or carbonates and organic bases such as mono-, di-, and triethanol-amines have been used for the past several years for the separation of carbon dioxide from these gases. However, these processes have not been capable of treating ammonia containing gases because substantial quantities of ammonia are dissolved in the absorbing solution and are evolved with the carbon dioxide when this solution is regenerated.

The Chemical Construction Corporation of United States is the first concern which claims to use aqueous solutions of monoethanolamine for the separation and separate recovery of ammonia and carbon dioxide. Their technique is well suited for the treatment of concentrated gas mixtures of the type encountered in urea manufacture. On the strength of their new technique, they have obtained a patent (7) for their process. It is claimed that a substantially complete separation of carbon dioxide from mixtures with ammonia can be obtained by a combined absorption and partial stripping of the aqueous absorbing solution, whereby contamination of enriched solution with substantial quantity of dissolved ammonia is prevented. In their preferred practice the enriched solvent from the absorbing stage is subjected to an initial heating, the extent of which is limited to that necessary to strip out or drive off the dissolved ammonia without, however, liberating more than a minor proportion of the absorbed carbon dioxide. The gases so liberated are returned to the

absorption stage, thus preventing any substantial loss of ammonia from the gases undergoing treatment. The partially stripped enriched solvent is then further heated in a regenerating stage with the result that most of its combined carbon dioxide is liberated as a substantially ammonia free carbon dioxide gas after which the regenerated solvent is cooled and returned to the absorption stage.

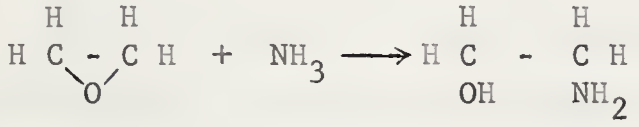
This type of separation is of considerable interest at the present time in view of the commercial importance of urea. The value of ammonia has stimulated an interest in separating and recirculating it during the urea synthesis. Reliable vapor liquid equilibria data of such aqueous systems of organic bases containing ammonia and carbon dioxide is therefore of paramount interest in the design of process equipment for the separation of ammonia and carbon dioxide.

II. THEORY AND PREVIOUS WORKS

The literature survey reported here summarizes the results obtained by other investigators on the absorption of carbon dioxide in ethanolamines and on the vapor pressures of ammonia and carbon dioxide in equilibrium with aqueous solutions.

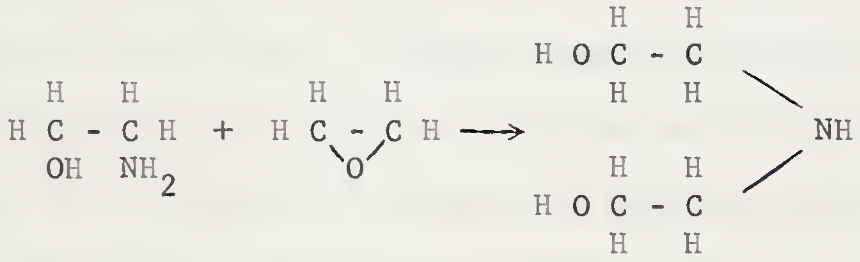
A. Monoethanolamine and its Aqueous Solutions

Monoethanolamine in its pure state is a viscous liquid with a slight ammoniacal odor. It is produced by reacting ethylene oxide with ammonia followed by fractional distillation to separate mono-, di-, and triethanolamine.



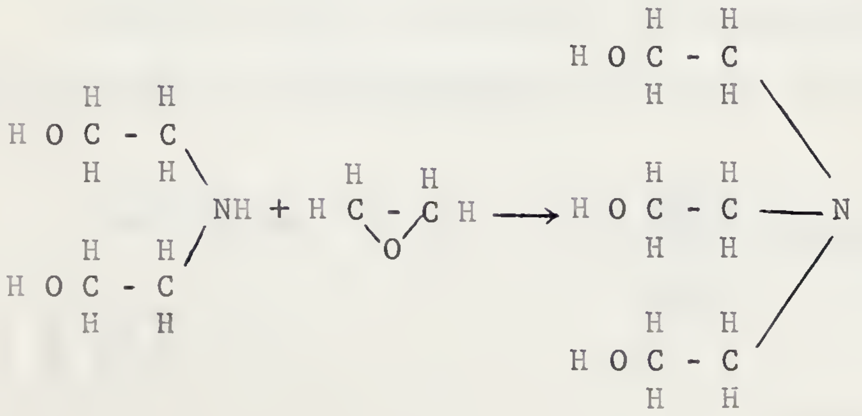
(1)

Monoethanolamine



(2)

Diethanolamine



(3)

Triethanolamine

Monoethanolamine is a highly hygroscopic substance. It dissolves in H_2O in all proportions to give a basic solution

$$HOCH_2CH_2NH_2 + HOH \longrightarrow HOCH_2CH_2\overset{+}{NH_3} + \overset{-}{OH} \qquad (4)$$

The pH of a 25% by weight monoethanolamine solution is 12.1. Monoethanolamine is a very corrosive substance as a consequence of its high reactivity with metals and oxygen. It is believed that the basic cause of severe corrosion results from traces of oxygen which may enter the scrubbing tower with the gas stream. Reactions of ethanolamine with oxygen yields aminoacetic acid which is very corrosive towards metal surfaces.

$$NH_2CH_2CH_2OH + O_2 \longrightarrow NH_2CH_2COOH + H_2O \qquad (5)$$

Aqueous solutions of monoethanolamine react readily with acid gases such as carbon dioxide and hydrogen sulphide and absorb these gases at moderate temperatures of 80^o - 120^oF and pressures ranging from atmospheric to 1000 psig. At high temperatures monoethanolamine solutions possess the property of being non alkaline with the result that amine carbonates and sulphides dissociate and hydrogen sulphide and carbon dioxide are readily volatilized from the solution.

There are three possibilities of the reactions involved between aqueous solution of monoethanolamine and carbon dioxide.

$$2\ HOCH_2CH_2NH_2 + H_2O + CO_2 \underset{300^oF}{\overset{120^oF}{\rightleftharpoons}} (HOCH_2CH_2NH_2)_2H_2CO_3 \qquad (6)$$

$$2\ HOCH_2CH_2NH_2 + H_2O + CO_2 \underset{300^0F}{\overset{120^0F}{\rightleftharpoons}} (HOCH_2CH_2NH_3)_2CO_3 \qquad (7)$$

$$(HOCH_2CH_2NH_3)_2CO_3 + H_2O + CO_2 \underset{300^0F}{\overset{120^0F}{\rightleftharpoons}} 2\ HOCH_2CH_2NH_3HCO_3 \qquad (8)$$

These are overall reactions and may not show a true picture of reaction mechanism.

B. Absorption of Carbon Dioxide by Aqueous Monoethanolamine Solutions

Bottoms' (4), experimental study of the problem of economic removal of carbon dioxide from gaseous mixtures culminated in the discovery of the use of ethanolamines for the removal of carbon dioxide and hydrogen sulphide. He disclosed the fact that certain amines and amino compounds have the property of absorbing carbon dioxide and hydrogen sulphide forming pyrolitically unstable carbonates and hydrosulphides which, when heated to a temperature above 50^0C decompose and liberate the carbon dioxide and hydrogen sulphide and release the free base in the original form. Bottoms gave data for 50% (by volume) solutions of tri-, and diethanolamines at 25^0, 35^0, 45^0 and 55^0C and at varying partial pressures of carbon dioxide up to a maximum of 760 mm Hg. He did not give any information on the experimental method that he used nor did he refer specifically to monoethanolamine.

The next important work in this connection was done by Mason and Dodge (6). They presented data on the equilibrium solubility of carbon dioxide in aqueous solutions of mono-, di-, and triethanolamines for partial pressures of carbon dioxide varying from 10 to 760 mm Hg. For each amine the data covers a range of temperature from 0^0C to 75^0C and a range of concentrations of the pure amine in water solution from

0.5 to 12.5 normality. Mason and Dodge attained equilibrium by bubbling the gas through the liquid. Their method of analysis of the liquid samples consisted of evolving carbon dioxide from the heated solution by the addition of acid, followed by the absorption of carbon dioxide in ascarite. To ensure against any change in weight of the ascarite tubes due to moisture, tubes containing calcium chloride and phosphorus pentoxide were placed ahead of the ascarite. The effluent gas phase was analyzed for carbon dioxide and water vapor using a similar absorption train.

Considerable difference exists between the data of Bottoms and that of Mason and Dodge. This is explained by the fact that the amines available during the time of Bottoms (4) were not as pure as during the time of Mason and Dodge (6).

C. Vapor Pressure of Ammonia and Carbon Dioxide in Equilibrium with Aqueous Solutions

The ammonia and carbon dioxide vapor pressures of solutions of these two gases having a constant ammonia content but with varying proportions of carbon dioxide have been examined at 20°, 30° and 40°C by Badger and Pexton (2). Solutions having an ammonia concentration of 0.128N, 0.5N, 1N and 2N were examined at both 20°C and 40°C, solutions of 1.5N at 20°C only, and 1N at 30°C. The effects of hydrogen sulphide (3) and ammonium choloride (1) in such solutions have also been studied by the same authors. The presence of hydrogen sulphide in the solutions indicated that the vapor pressures of ammonia and carbon dioxide over the solutions were in agreement with the assumption that the whole of

hydrogen sulphide could be regarded as having combined with half its equivalent of ammonia and that the resulting ammonium hydro sulphide has no effect on the partial vapor pressure of the remaining ammonia and carbon dioxide.

In the presence of ammonium chloride in such solutions, the ammonia vapor pressure appeared to be raised by an amount independent of ammonia concentration but dependent on the ratio of $CO_2:NH_3$. The effect of ammonium chloride on the vapor pressures of carbon dioxide was relatively greater, but no constant difference was observed. When sodium chloride was used in place of ammonium chloride, the vapor pressures of ammonia and carbon dioxide were slightly lowered.

The reason as to why ammonium chloride caused slight rise in the ammonia vapor pressure and considerable rise in the carbon dioxide vapor pressure was explained by considering the ionic equilibria involved in the liquid phase.

These are:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \qquad (9)$$

$$HCO_3^- \rightleftharpoons CO_3^= + H^+ \qquad (10)$$

$$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^- \qquad (11)$$

$$NH_3 + HCO_3^- \rightleftharpoons NH_2COO^- + H_2O \qquad (12)$$

It is evident from Eqn. (11) that an increase in the amount of NH_4^+ would increase the amount of NH_3 in the gas phase. But an increase

in the acidity of solution due to NH_4Cl tends to decrease the ammonia concentration in the gas phase. The net result is a small increase in NH_3 vapor pressure. Similarly the increase in hydrogen ion increases the amount of CO_2 in the gas phase as it is evident from Eqn. (9). The only counter balancing force for this increase is a slight fall in HCO_3^- which combines with some of the increased ammonia to form more carbamate.

III. EXPERIMENTAL METHODS

A. General

There are various standard methods of obtaining vapor liquid equilibria. The design of a particular apparatus depends on the temperature and pressure range and also on the type of system under investigation. In principle, the apparatus can be classified into two categories depending on whether the dynamic or static method of vapor liquid equilibrium determination is used.

In the dynamic method a vapor is passed through a series of vessels containing liquid of a suitable composition. The vapor entering the first vessel may be of a composition somewhat different from the equilibrium vapor, but as it passes through the system it tends to approach equilibrium. The number of vessels employed should be such that the vapor entering the last unit is of essentially equilibrium composition.

This system has the advantage that it is simple and, in certain cases, it is possible to dispense with the analysis of the liquid sample, i.e., the liquids can be made of a known composition, and since the change in the last vessel is small, it is possible to assume that the composition of the liquid in this case is equal to that originally charged.

It is obvious that it cannot be an exact equilibrium system because of the fact that a pressure drop is involved in passing the vapor through the system; i.e., there are pressure variations which will affect equilibrium. There is also danger of entrainment, although this can be minimized by low velocities.

In a great many cases, the gas introduced into the first vessel has been carrier gas of low solubility and not a component of the system. Thus, in the determination of the vapor-liquid equilibria for systems such as ammonia and water, ammoniacal solutions are placed in the vessels, and a gas such as nitrogen is bubbled into the first of these and the resulting nitrogen-ammonia-water vapor mixture is passed through the succeeding vessels obtaining a closer approach to equilibrium. Equilibrium obtained in such a manner is not the true vapor-liquid equilibria for the water vapor-ammonia system. It closely approaches true equilibrium for the binary system under a total pressure equal to the partial pressure of the ammonia and the water vapor in the gaseous mixture. Even this is not exact. The carrier gas has some solubility in the liquid phase, and the partial pressure of these added constituents modifies the energy relations of the liquid and vapor phases. Usually for low-pressure operation these errors are not large in magnitude, but as the pressure becomes higher the errors are serious and the method can give erroneous results if the true vapor-liquid equilibria for mixtures without the carrier gas are desired.

In the static method, the liquid sample is placed in a closed evacuated vessel and then measured amount of gases are introduced into it. It is then agitated by rocking, or by other means, at constant temperature until equilibrium is obtained between the vapor and the liquid.

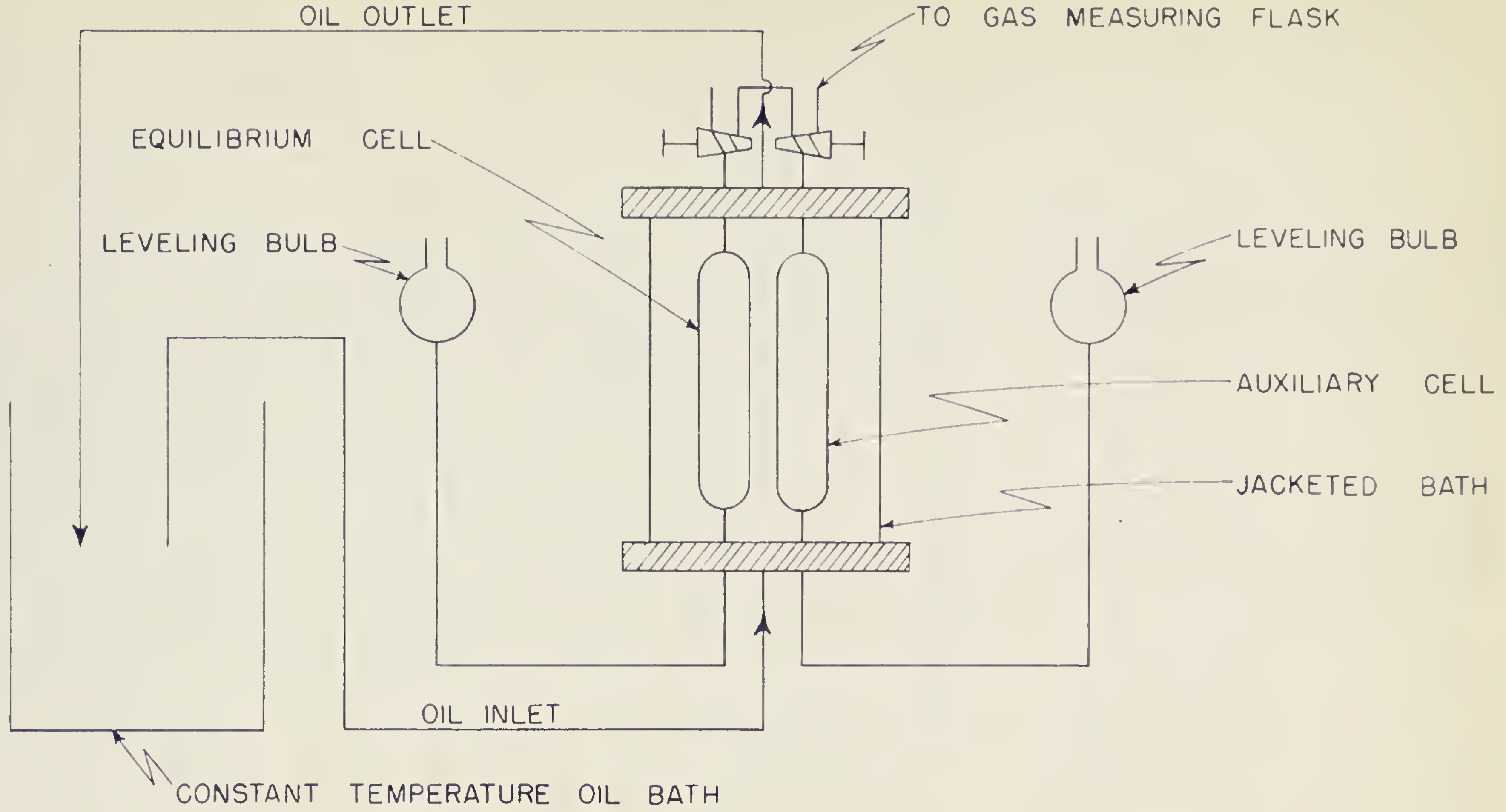
The method appears simple, but it involves certain difficulties. During sampling there are pressure changes due to the removal of the material, and these pressure changes can be large in magnitude. In

order to avoid them, it is customary to add some fluid, such as mercury, to the system while the samples are being removed in order to prevent any vaporization or condensation.

The system under investigation created a particular problem because ammonium carbamate sublimation from the gas phase had to be avoided. A special equilibrium apparatus having some new features had to be designed in order to prevent this.

B. Equilibrium Cell

In the design of the cell as shown in Fig. 2, particular attention was paid to the fact that the contents of the cell should always be visible. This was essential because the level of mercury in the cell had to be frequently adjusted to bring the pressure inside the cell to atmospheric. As may be seen from Fig. 1, this was achieved by raising or lowering the leveling bulb connected to the equilibrium cell until the two mercury levels were the same. This point was determined by using a cathetometer. There were two cells of the same size and capacity, one was the equilibrium cell and the other was for storing the gas phase before transferring it to the analyzing vessel. The main features of the two cells were very simple, each made of pyrex glass tube 8 inches long and 350 cc capacity. Both cells were included in a jacketed vessel, the main body of which was a 12 inches long and 6 inches inside diameter glass cylinder. The glass cylinder along with its aluminum flanges was supplied by Corning Glass Co. The glass cylinder was closed on both ends with stainless steel discs supported by aluminum flanges and rubber gaskets. The top end of the two cells were joined by two high vacuum stopcocks. The lower end of the two cells were connected


OIL OUTLET
TO GAS MEASURING FLASK
EQUILIBRIUM CELL
LEVELING BULB
LEVELING BULB
AUXILIARY CELL
JACKETED BATH
OIL INLET
CONSTANT TEMPERATURE OIL BATH

SCHEMATIC APPARATUS ASSEMBLY

FIGURE I

to the two leveling bulbs filled with mercury. The portion of the cells above the jacketed vessel was kept heated by passing measured amount of current in the insulated nichrome wire around the glass tubing. Current in the nichrome wire was controlled by passing it through a variable transformer and an ammeter in series so that the line did not get over heated.

The jacketed equilibrium cell in Fig. 2 was mounted on a central axis to a frame. The jacketed vessel thus could be rotated about a central axis so that the contents of the cell could be thoroughly and easily agitated.

C. Measurement and Control of Phase Variables

(i) Temperature

The temperature of the equilibrium cell and its contents was controlled by controlling the temperature of a Semtol oil which was circulated from an auxiliary constant temperature bath in Fig. 1 through the jacket enclosing the cell. The oil entered the jacket on one side at the bottom and left on the opposite side at the top. This method of circulation of oil gave thorough agitation inside the jacket.

The auxiliary temperature bath was a small cork insulated porcelain tank filled with Semtol oil. An immersion pump mounted in the tank continuously circulated the oil. The temperature of the oil in the tank was controlled by passing the current in a 700 watt heater through a microset thermoregulator and an electronic control box. In this way the temperature of the bath could be controlled to within about $\pm$ 0.1°F. The temperature within the cell was measured by mercury in glass thermometer immersed into the bath surrounding the cells.

(ii) Pressure

The pressure inside the cell was always kept at atmospheric. This was done by raising or lowering the leveling bulb in Fig. 1 connected to the equilibrium cell. The level of mercury in the cell and that in the leveling bulb were brought to the same point by using the cathatometer. The barometric pressure at that time was the pressure in the cell.

D. Experimental Technique

First the two cells and the glass tubing connecting them were filled with mercury by raising the two leveling bulbs. A dropping funnel was then connected to the equilibrium cell in Fig. 1 and after the mercury level was brought one inch inside the funnel stem, a measured quantity of aqueous solutions of monoethanolamine was introduced into the funnel. By lowering the leveling bulb the solution along with the mercury column was brought inside the cell and then the stopcock was closed.

After the solution was transferred inside the equilibrium cell, the circulation of oil from the constant temperature bath was started to bring the desired temperature in the cell. When the desired temperature was reached, a measured amount of carbon dioxide and ammonia were introduced into the cell by two gas measuring burettes. The transferring line between the burettes and the equilibrium cell was evacuated before transferring the gases. While introducing the gases, the equilibrium cell was constantly shaken, otherwise hours would be needed for the gases to go into the solution. In the last stage of absorption, care was taken that no excess gases were introduced since the capacity of the cell was limited and also because while shaking, the solution absorbed more gases than needed for equilibrium absorption and then started releasing them after

the shaking was stopped.

After the desired amount of gases were introduced in the equilibrium cell, the gas measuring burettes were disconnected. A thorough shaking was then needed to bring the gases and liquid to equilibrium. Without efficient shaking arrangement, hours would be needed to bring carbon dioxide and ammonia into true equilibrium.

Once the level of mercury in the equilibrium cell and that in the leveling bulb were equal for some time, it was assumed that the gases and liquid inside the cell were at equilibrium.

After the equilibrium was attained, the rubber tubings connecting the two cells and the leveling bulbs were compressed tightly under a Jumbo Hosecock Compressor in Fig. 2. Thus without disturbing the conditions inside the equilibrium cell, the leveling bulb connected to the equilibrium cell was raised to a high position and that connected to the auxiliary cell was lowered. After the stopcock of the equilibrium cell was opened towards the auxiliary cell, the hosecock was slowly opened in such a way that the mercury level inside the equilibrium cell started rising and that in the auxiliary cell started falling both at the same speed. The speed of the mercury columns was checked by the graduation marks on the two cells. After all the gas phase was transferred inside the auxiliary cell, the stopcock of it was closed. The gas phase in the auxiliary cell was then ready for analysis.

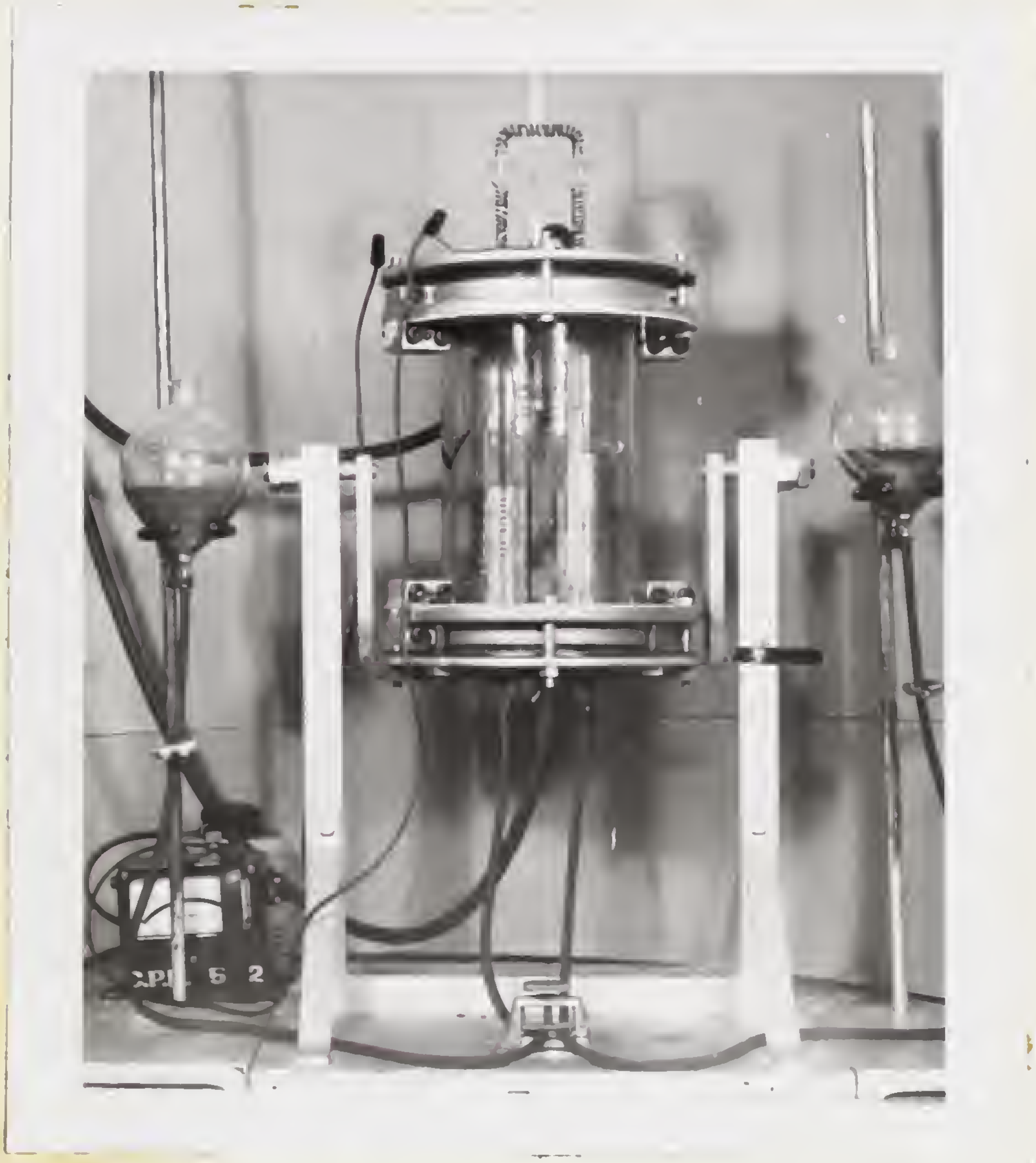


Figure 2

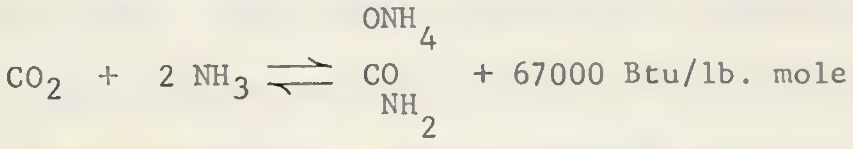
IV. ANALYTICAL METHOD

After a careful study of all the known procedures of gas analysis, it was found that the analysis of a mixture of gases having ammonia, carbon dioxide and water vapor was somewhat difficult. No solid absorbent was found for water vapor in which ammonia is not also absorbed, specially in the presence of water vapor. In all similar previous investigations, water vapor was calculated from Raoult's law and therefore no attempt was made to find it analytically.

The method adopted in this case was to find the total number of moles first and then subtract from it the moles of ammonia and carbon dioxide to find the moles of water vapor.

A. Total Number of Moles

The most important consideration governing the handling of the gas mixtures was that they should never be permitted to exist at a condition where carbamate could form.



$$CO_2 + 2\ NH_3 \rightleftharpoons \begin{matrix} ONH_4 \\ CO \\ NH_2 \end{matrix} + 67000\ \text{Btu/lb. mole} \qquad (13)$$

Ammonium carbamate
(solid)

Solid carbamate has dissociation pressure of about one atmosphere at 60°C and then 7 atm. at 100°C. At pressures higher than the corresponding dissociation pressure, carbamate is readily formed, with substantial liberation of heat. In order to measure the total number of moles, the gases were expanded into an evacuated flask in Fig. 3 in a constant temperature water bath which permitted visual observation of the flask contents. The expansion was made to such a temperature and pressure

condition that no carbamate reaction was possible.

The volume of the flask was first determined very carefully by weighing the flask with and without water. Knowing the weight and density of water at that temperature, the volume of the flask was calculated. The flask was then connected to a U tube mercury filled manometer capable of reading pressure up to 160 mm Hg. One end of this manometer was sealed and the other end was open. The flask along with the manometer in Fig. 3 was placed in a constant temperature water bath maintained at 110.8°F. The pressure inside the flask was always made between 80 - 130 mm Hg.

To avoid any carbamate reaction, the transferring line between the auxiliary cell and the flask was kept heated by a heating tape. The flask and the line connected to the auxiliary cell were first evacuated to a pressure of 10^{-2} mm Hg by opening the stop-cock No. 4 towards the high vacuum oil pump. Once the desired vacuum was reached, stop-cock No. 1 was closed and the stop-cock of the auxiliary cell was then opened towards the flask. After all the gases were transferred from the cell into the flask, the stop-cock of the cell and the stop-cock No. 3 were closed. The stop-cock No. 2 was then opened towards the manometer and the pressure was read after it was steady for some time. The total number of moles was then calculated from the ideal gas law. The application of the ideal gas law was justified because the pressure in our case was never more than 130 mm Hg and also because the temperature was quite high.

B. Analysis of Ammonia and Carbon Dioxide

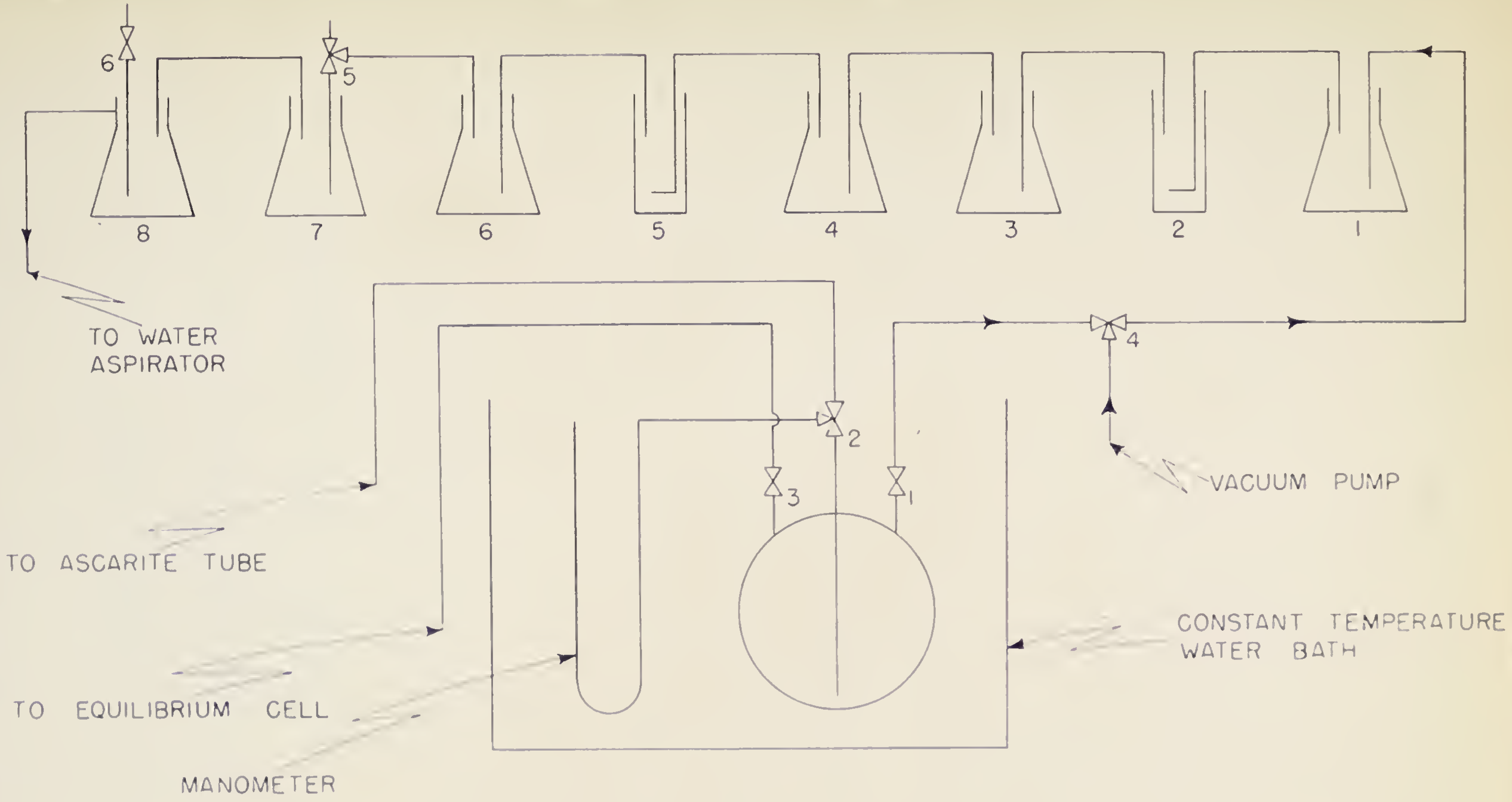
By opening the stop-cock No. 2 towards the tube filled with ascarite and anhydrous calcium sulphate, a slow stream of air was passed

into the flask. After the contents of the flask were at atmospheric pressure, the stop-cock No. 1 and the stop-cock No. 4 were opened towards the absorption train and the suction was started in the line by the water aspirator. The flow rate of the gases through the absorption train was regulated by operating the stop-cock No. 6. Care was taken that the absorption rate be very slow.

In the absorption train, the absorption bottle No. 2 in Fig. 3 was filled with 50 cc of 0.1N H_2SO_4 and a drop of methyl orange as indicator for the absorption of ammonia. For the absorption of carbon dioxide, the absorption bottle No. 5 was filled with 50 cc of 0.1N NaOH along with 15 cc of 10% $Bacl_2$ solution (5) and a drop of phenolphthelein as indicator. The conical flasks No. 3 and 6 filled with 10 cc of $0.1NH_2SO_4$ and 0.1N NaOH respectively were used just for precautionary measure so that in case some gases escaped the absorption bottles No. 2 and No. 5, they must get absorbed in these bottles. Conical flasks No. 1 and No. 4 were used as precautionary measure from back suction. The total time of purging the suction line from air for complete absorption was two hours. After one and a half hours of purging was done, the stop-cock No. 2 was closed and then the last half hour of purging was completed by opening the stop-cock No. 3 towards the ascarite tube. As recommended by Dickson and Jay (5), the sulphuric acid bottles were heated to boiling during the last 15 minutes of purging to drive out any carbon dioxide that got absorbed in H_2SO_4 which has a finite capacity for that at room temperature.

After the purging was complete, the suction line was stopped by closing the stop-cock No. 5 first and then the water aspirator. After a

few minutes of waiting, the sulphuric acid bottles were taken out and back titrated with 0.1N NaOH for determining the ammonia content of the gas phase. Carbon dioxide was determined by back titrating the NaOH solutions with 0.1N HCl.


6
5
8
7
6
5
4
3
2
1
TO WATER ASPIRATOR
4
2
3
1
VACUUM PUMP
TO ASCARITE TUBE
CONSTANT TEMPERATURE WATER BATH
TO EQUILIBRIUM CELL
MANOMETER

SCHEMATIC OUTLINE OF ABSORPTION TRAY FOR CO_2 AND NH_3

FIGURE 3

IV EXPERIMENTAL RESULTS

The principal object of this phase of research was to display the mutual influence of carbon dioxide and ammonia in their absorptions in the aqueous solutions of monoethanolamine. There are two stages of absorption for both ammonia and carbon dioxide in such solutions. The primary absorption of carbon dioxide is due to the chemical reactions between carbon dioxide and monoethanolamine and then there is a secondary absorption of carbon dioxide which is governed by the chemical interactions between ammonia and carbon dioxide. Similarly the primary absorption of ammonia is due to water in the solution and then the secondary absorption depends on chemical interactions between ammonia and carbon dioxide.

Some of the major reactions involved in such solutions are as follows:

$$HOCH_2CH_2NH_2 + H_2O \rightleftharpoons HOCH_2CH_2NH_3^+ + OH^- \quad (14)$$

$$CO_2 + H_2O \rightleftharpoons 2H^+ + CO_3^= \quad (15)$$

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^- \quad (16)$$

$$HOCH_2CH_2NH_3^+ + HCO_3^- \rightleftharpoons HOCH_2CH_2NH_3HCO_3 \quad (17)$$

$$2\ HOCH_2CH_2NH_3^+ + CO_3^= \rightleftharpoons (HOCH_2CH_2NH_3)_2CO_3 \quad (18)$$

$$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^- \quad (11)$$

$$NH_3 + HCO_3^- \rightleftharpoons NH_2COO^- + H_2O \quad (12)$$

Experimental results of 1N, 5N and 9N monoethanolamine solutions at atmospheric pressure and temperatures 70° and 80°C and a few data of 5N monoethanolamine solution at 90°C are recorded in Tables I to XII in the Appendix. The ratio of CO_2:NH_3 by moles in the solution was calculated on pure water basis by subtracting the amount of carbon dioxide needed to react with monoethanolamine at a total pressure of one atmosphere from the total amount of carbon dioxide in the solution. The amount of carbon dioxide needed to react with monoethanolamine at total pressure of one atmosphere was found experimentally which is recorded in Table I. This value of carbon dioxide needed to react with 1N, 5N and 9N monoethanolamine solutions was compared at 70°C with the value of Mason & Dodge (6) by extrapolating their data. The value of Mason and Dodge appeared slightly lower in each case. The partition factor of ammonia which is the ratio of moles of ammonia per 1000 gm. of water in solution to moles of ammonia per litre of gas, was calculated by subtracting the amount of monoethanolamine from the total amount of the original solution in the cell. The partition factor for carbon dioxide was also found in the same way. Specific gravities of aqueous solutions of monoethanolamine at different concentrations are given in Table I.

The results in some useful forms are plotted in Figures 4 to 21. As it is evident from Figures 4 and 5, the partition factor of ammonia increases with the increase of the ratio CO_2:NH_3 and also with the increase of the normality of the solutions. The partition factor of carbon dioxide as shown in Figures 6, 7 and 8 increases first with the rise of the ratio CO_2:NH_3 and then decreases for most of the part. The plots in Figures 9, 10 and 11 show that the partial pressure of ammonia decreases but that of carbon dioxide increases with the rise of ratio CO_2:NH_3 and also with the rise of temperature.

FIGURE 4

PARTITION FACTOR OF NH_3 OVER AQUEOUS SOLUTIONS OF MONOETHANOLAMINE CONTAINING NH_3 AND CO_2 AT 70° C.

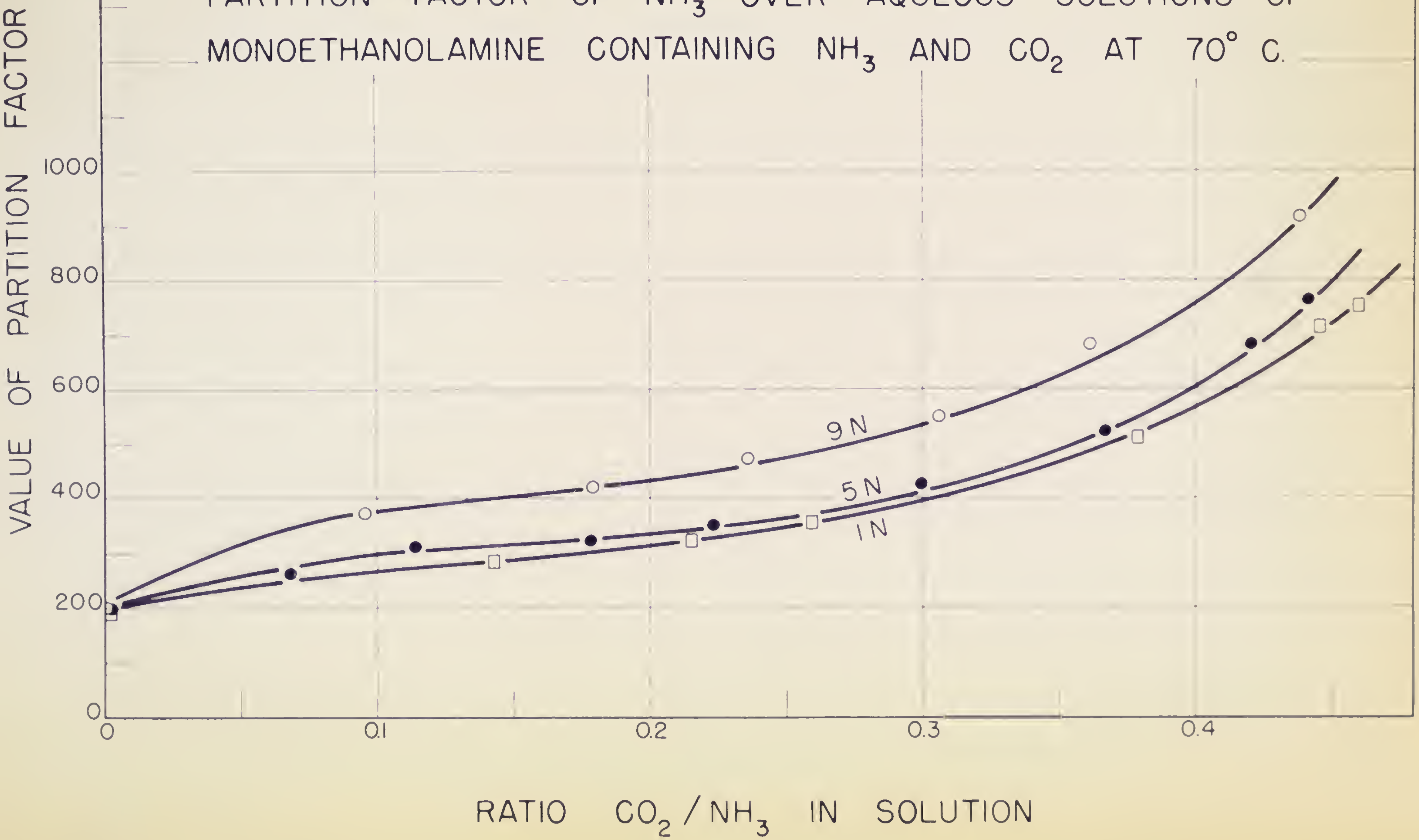
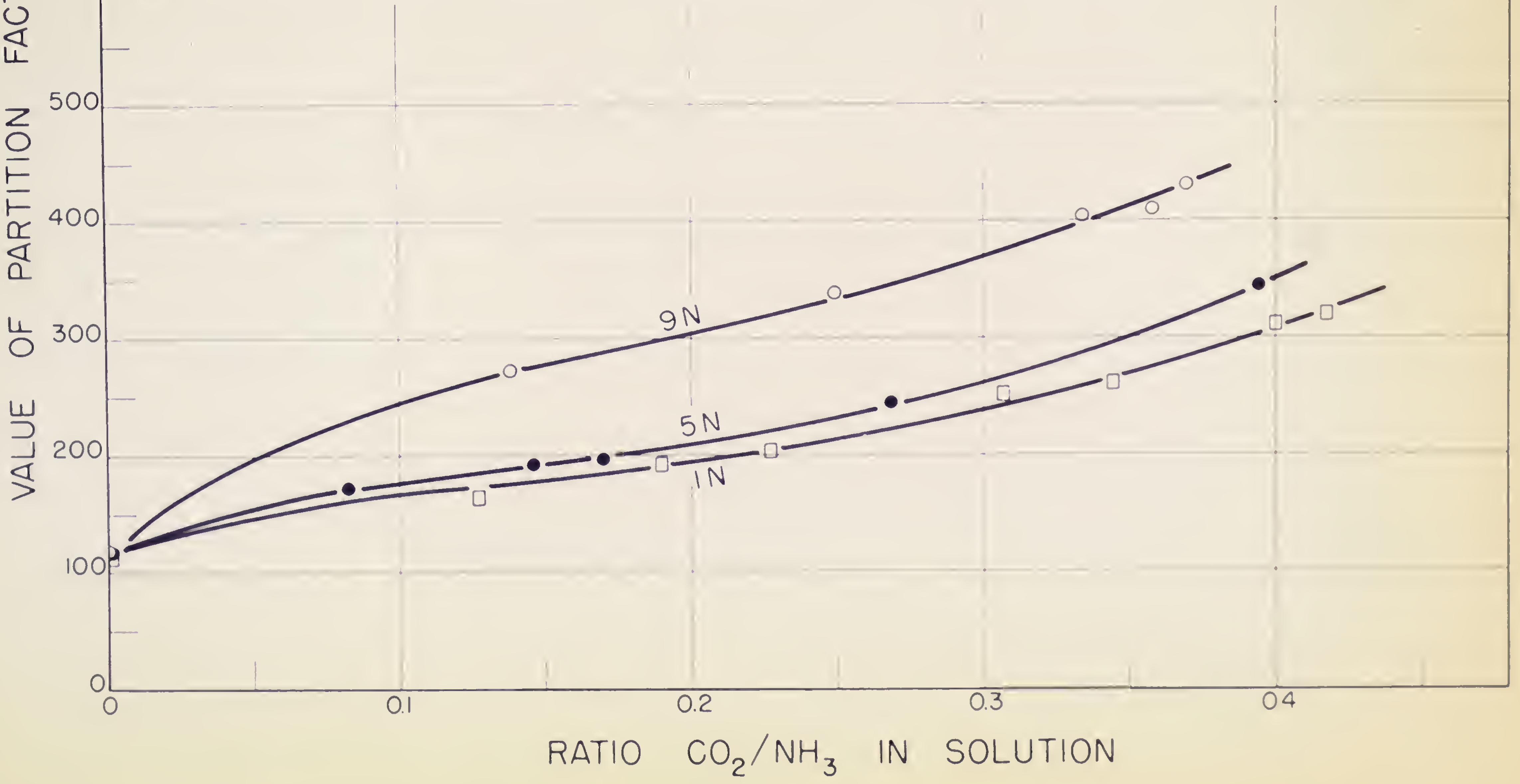


FIGURE 5

PARTITION FACTOR OF NH_3 OVER AQUEOUS SOLUTIONS OF MONOETHANOLAMINE CONTAINING NH_3 AND CO_2 AT 80° C.



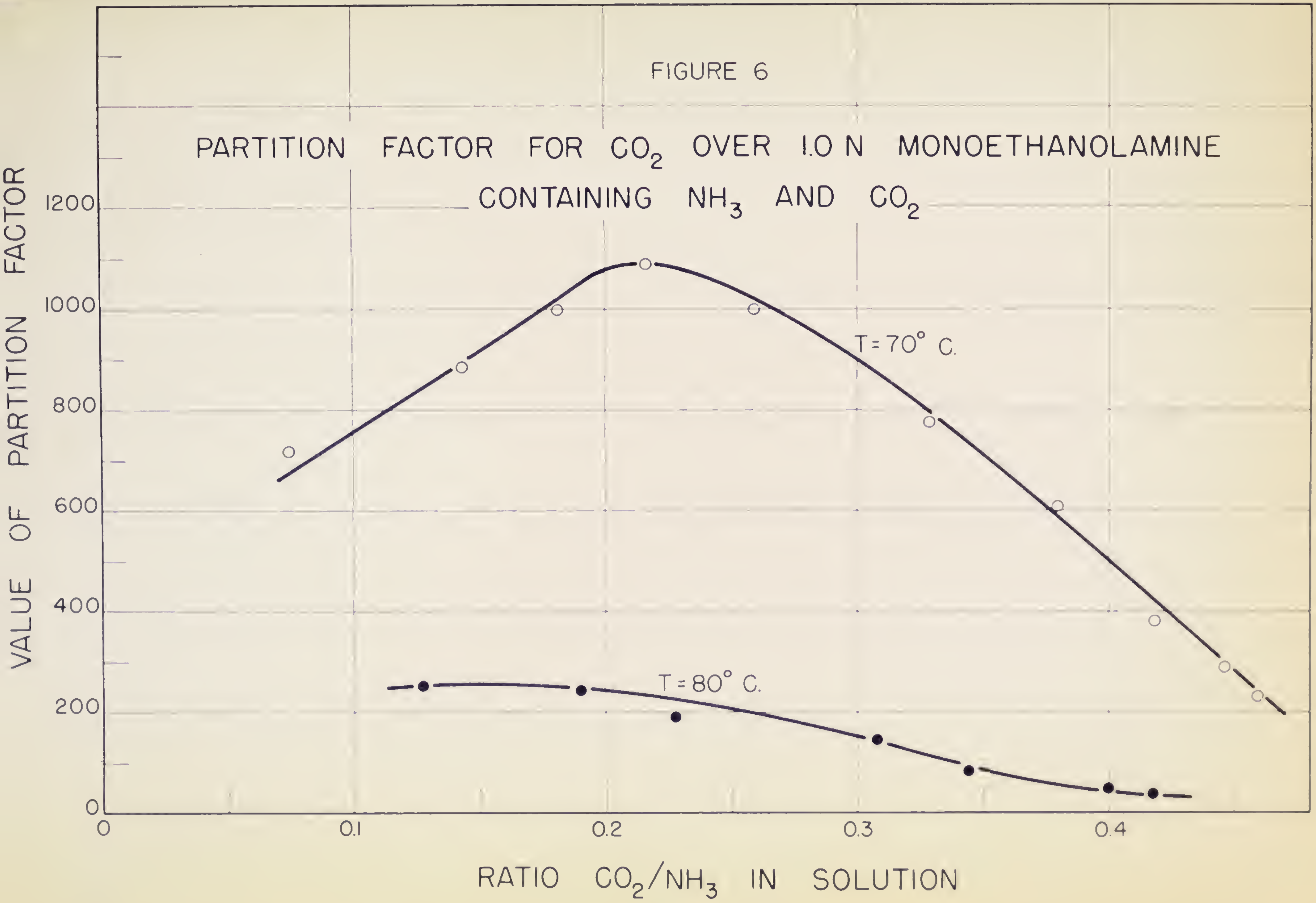


FIGURE 6

PARTITION FACTOR FOR CO_2 OVER 1.0 N MONOETHANOLAMINE CONTAINING NH_3 AND CO_2

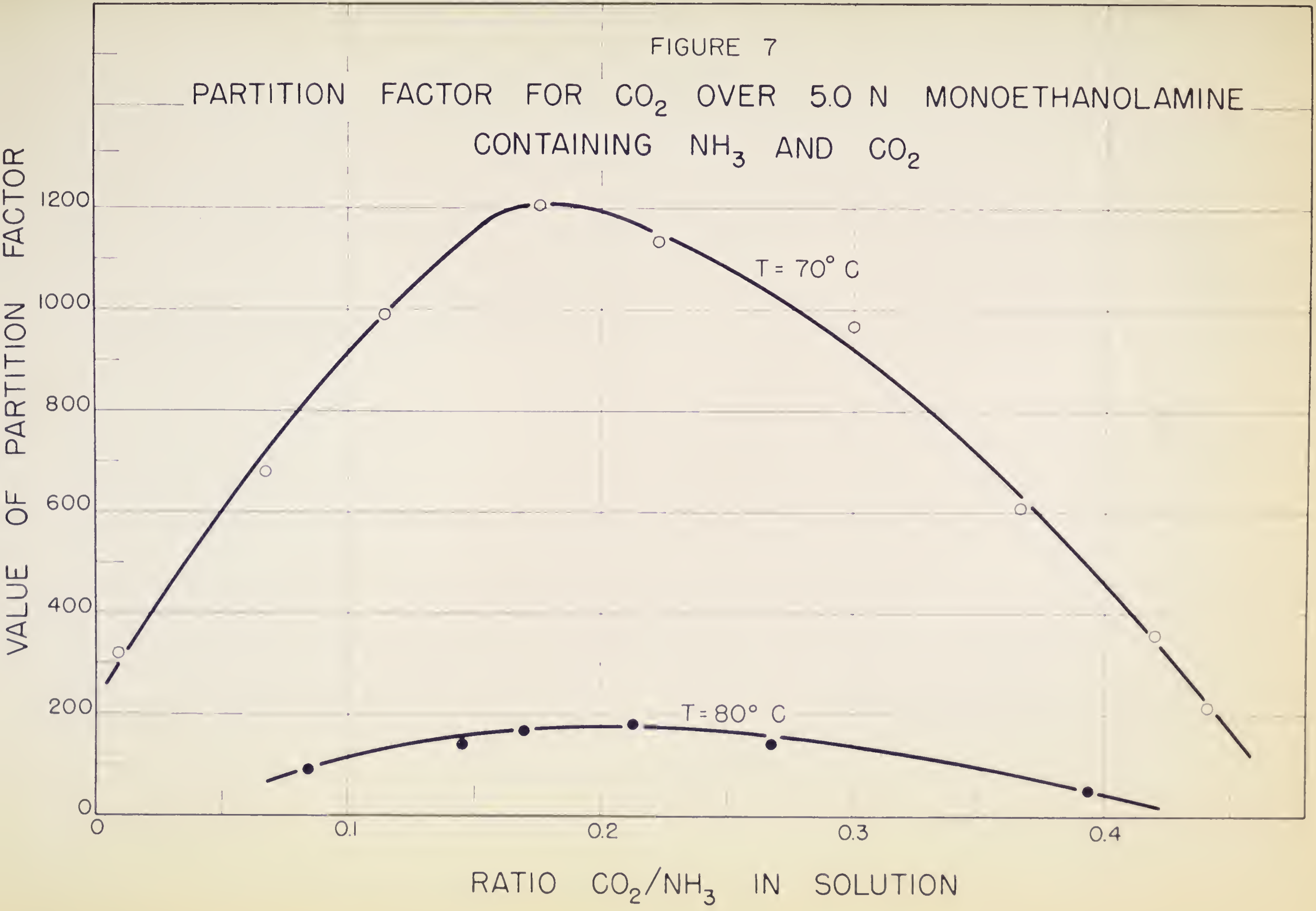


FIGURE 7

PARTITION FACTOR FOR CO_2 OVER 5.0 N MONOETHANOLAMINE CONTAINING NH_3 AND CO_2

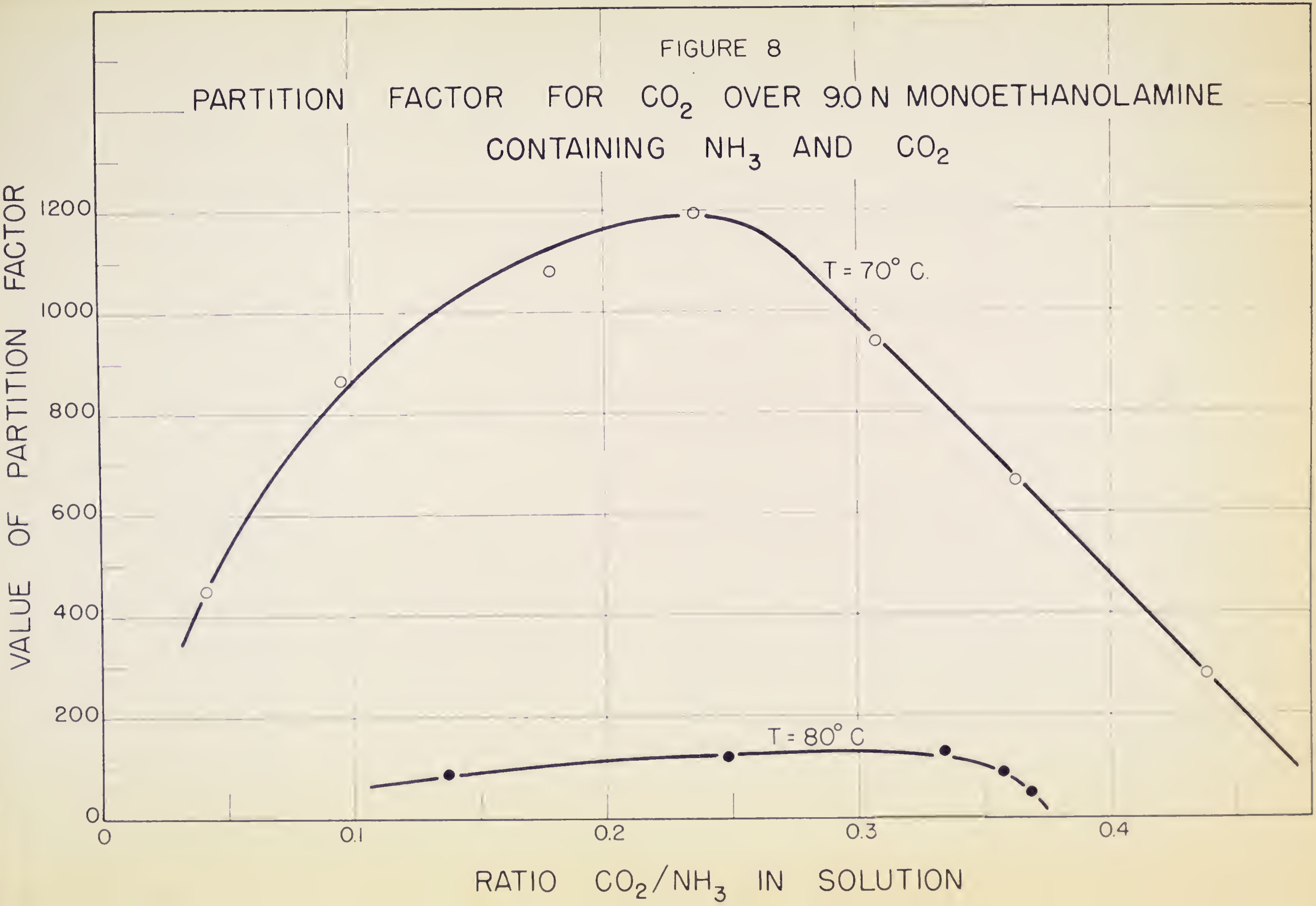


FIGURE 8

PARTITION FACTOR FOR CO_2 OVER 9.0 N MONOETHANOLAMINE CONTAINING NH_3 AND CO_2

The partial pressure of water vapor calculated from Raoult's law appeared much higher than the experimental value found analytically and this difference was more prominent at 80°C than at 70°C. Both value of partial pressures are given in Table X.

A plot of molality of ammonia versus partial pressure of ammonia for 1N, 5N and 9N monoethanolamine solutions at 70° and 80°C are shown in Figures 14 and 15. The numbers beside each point in Figures 14 and 15 indicate the molal ratio of CO_2:NH_3 in the solution. These plots were made particularly to analyze the data with respect to Henry's law. From the nature of the points in Figures 14 and 15, it is evident that the partial pressure of ammonia is not controlled entirely by the molality of the ammonia in the solution but it is also significantly influenced by the ratio of CO_2:NH_3 in the solution. For the same molality of ammonia, the partial pressure of ammonia differs widely at different ratios of CO_2:NH_3.

The nature of the points in Figures 14 and 15 are such that it is most probable that if the ratio CO_2:NH_3 be considered as a parameter then each point might be joined to the origin of the graph by a series of such points obtained experimentally at the same ratio. This is shown in Figures 17 and 18 by the dotted lines for 1N monoethanolamine. Such points for each ratio of CO_2:NH_3 may only be obtained by changing the total pressure of the system. Further work will be required in order to confirm and properly locate these curves.

It is most interesting to note that the experimental points in the highly carbonated region fall on a straight line drawn from the origin of the graph as shown by the solid line in Figures 16 and 17 for 1N

monoethanolamine solution. By this indication from the experimental results, it can be safely said that Henry's Law does hold for ammonia in the highly carbonated region. It is also evident from Figures 14 and 15 that this value of high carbonation decreases with the increase in temperature and also with the increase of the normality of the solutions.

The plots of partial pressure of carbon dioxide versus its molality in 1N, 5N and 9N monoethanolamine solutions are shown in Figures 18 and 19. The nature of the curves in this case are opposite to that of ammonia in the sense that the points in the region of lower ratios of CO_2:NH_3 appear to fall on straight line drawn from the origin of the graph. This ratio of CO_2:NH_3 decreases with the increase in temperature and also with the increase of normality of solutions. In the case of carbon dioxide, Henry's Law apply in the region of lower ratio of CO_2:NH_3 as shown by the solid line in Figures 20 and 21 for 1N monoethanolamine solutions.

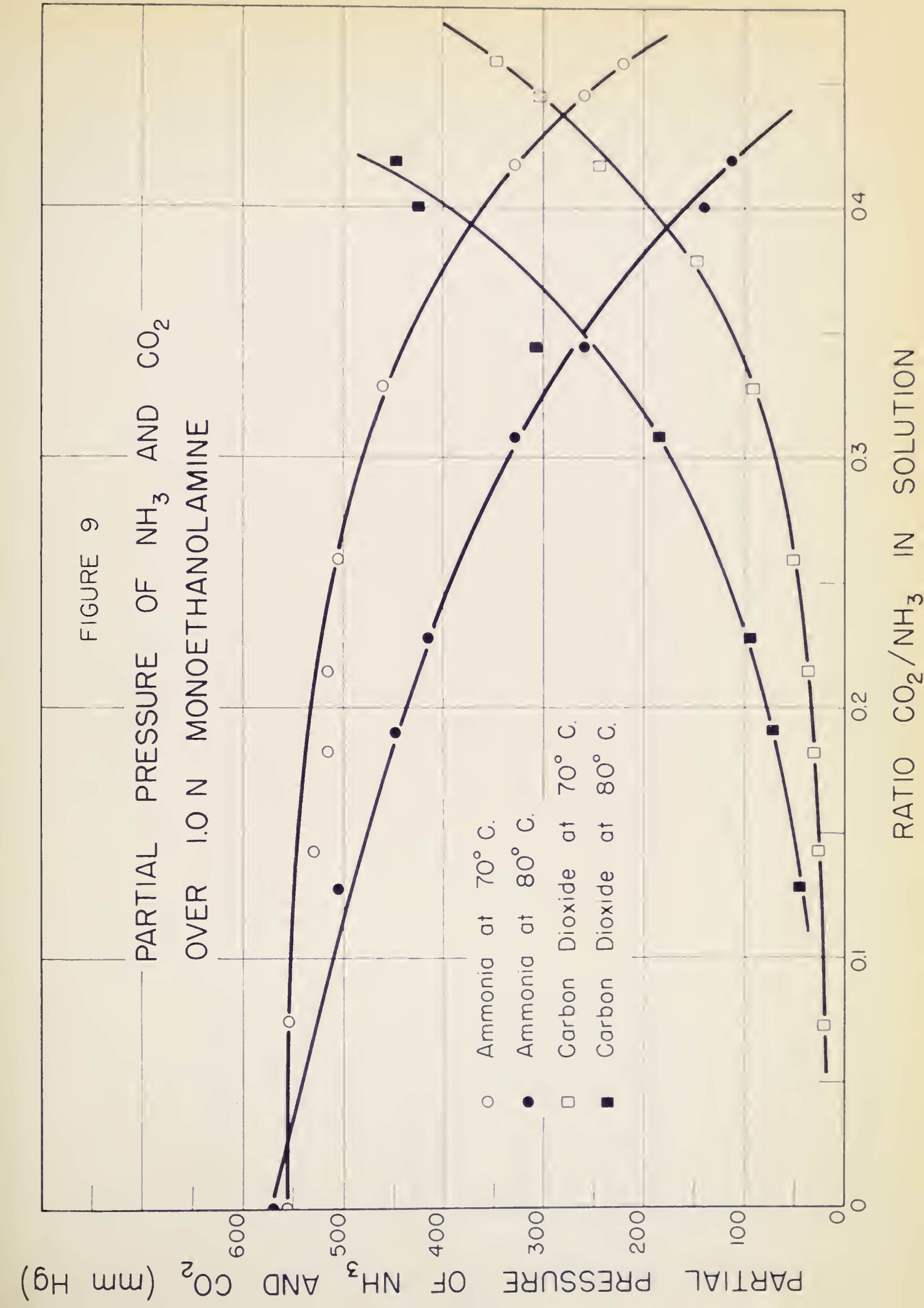


FIGURE 9

PARTIAL PRESSURE OF NH_3 AND CO_2 OVER 1.0 N MONOETHANOLAMINE

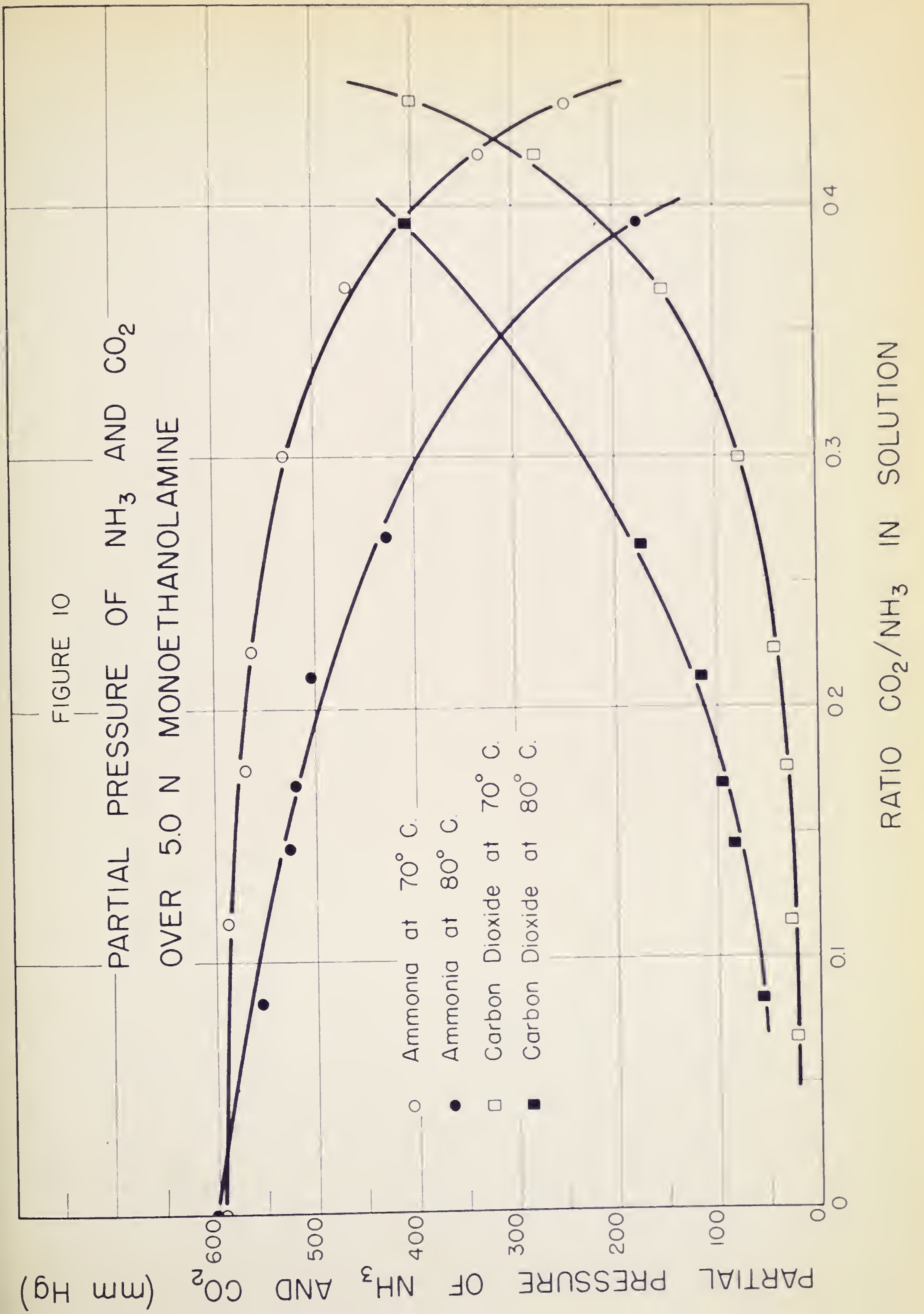


FIGURE 10

PARTIAL PRESSURE OF NH_3 AND CO_2 OVER 5.0 N MONOETHANOLAMINE

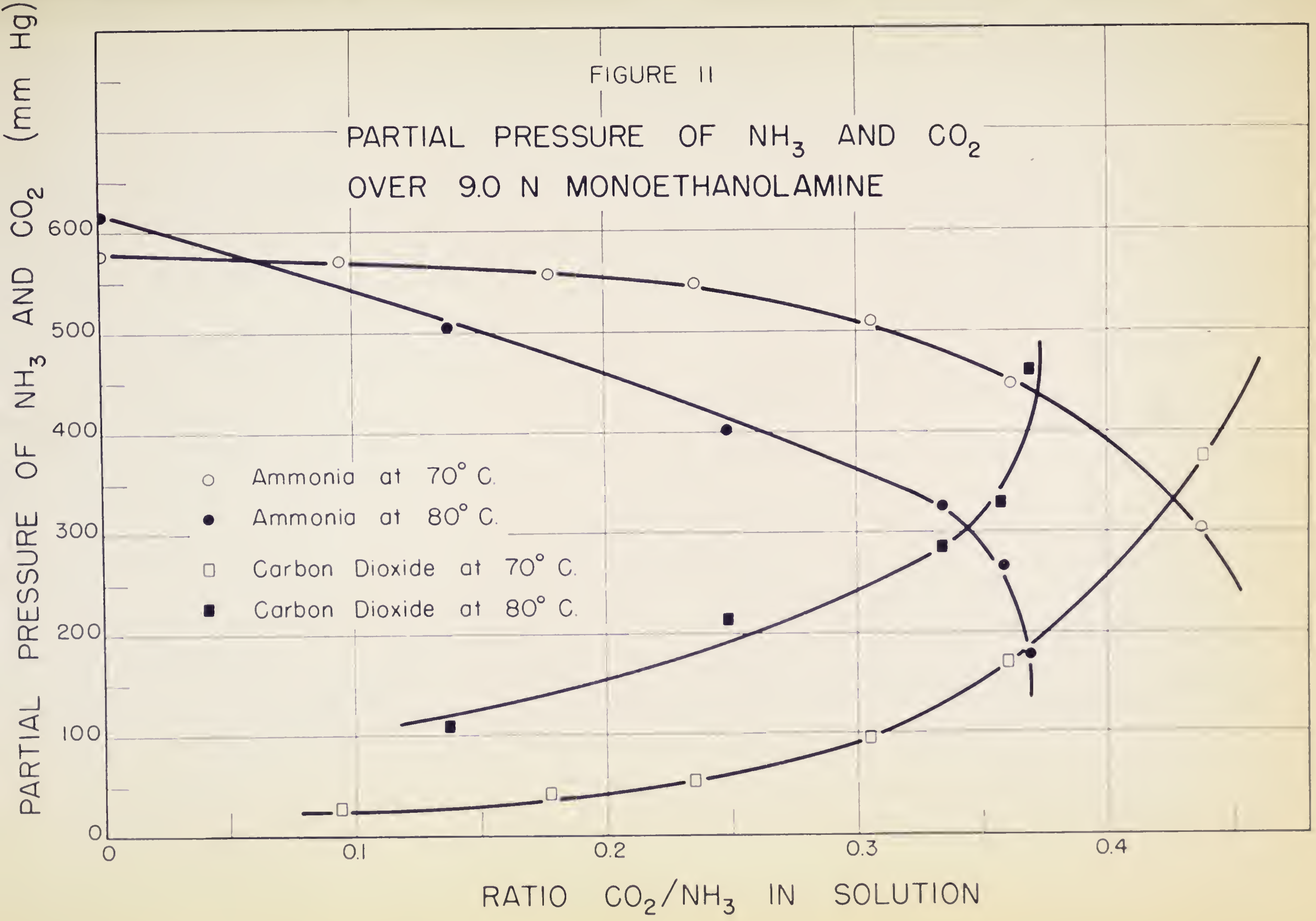


FIGURE 11

PARTIAL PRESSURE OF NH_3 AND CO_2 OVER 9.0 N MONOETHANOLAMINE

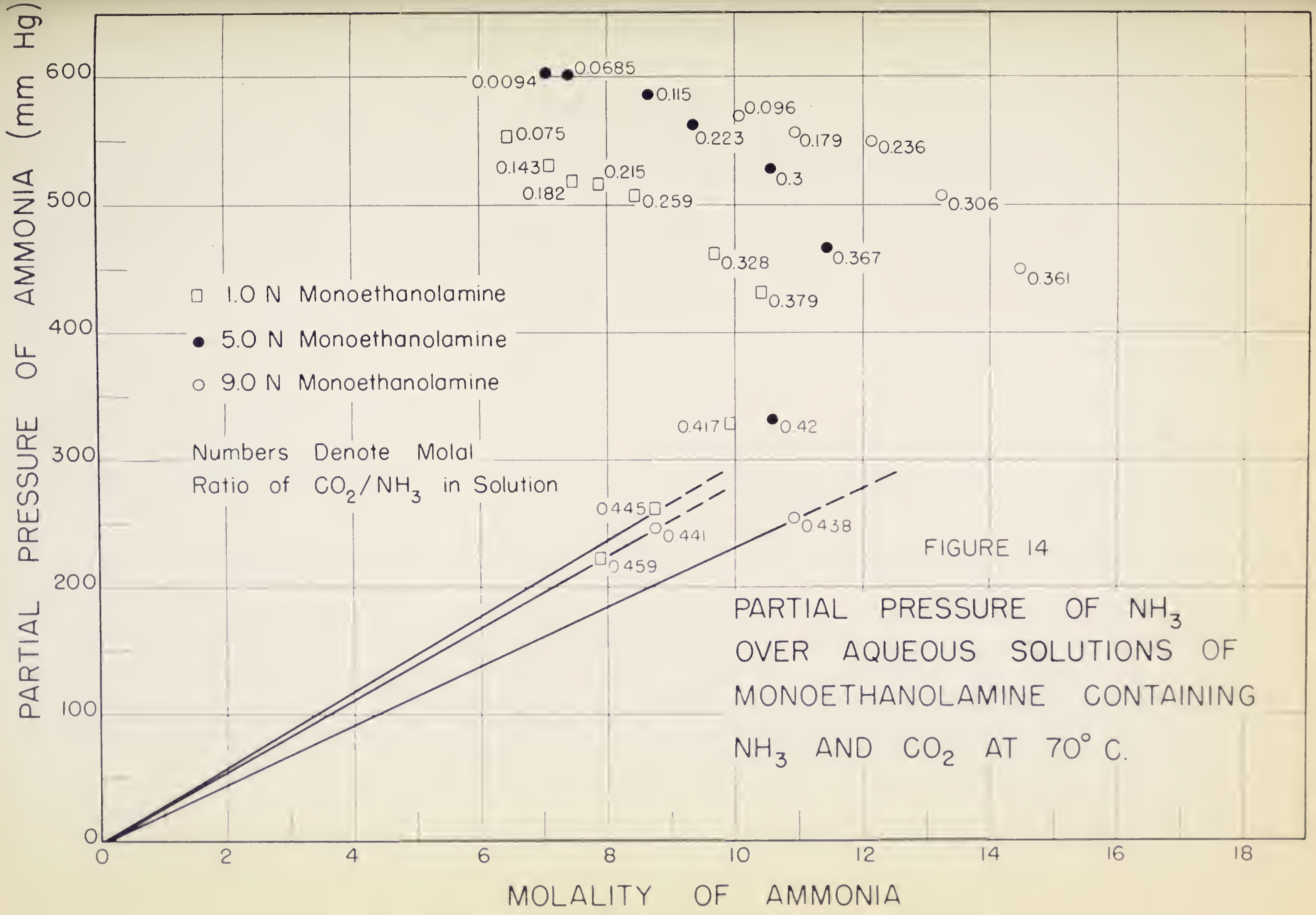


FIGURE 14

PARTIAL PRESSURE OF NH_3 OVER AQUEOUS SOLUTIONS OF MONOETHANOLAMINE CONTAINING NH_3 AND CO_2 AT 70° C.

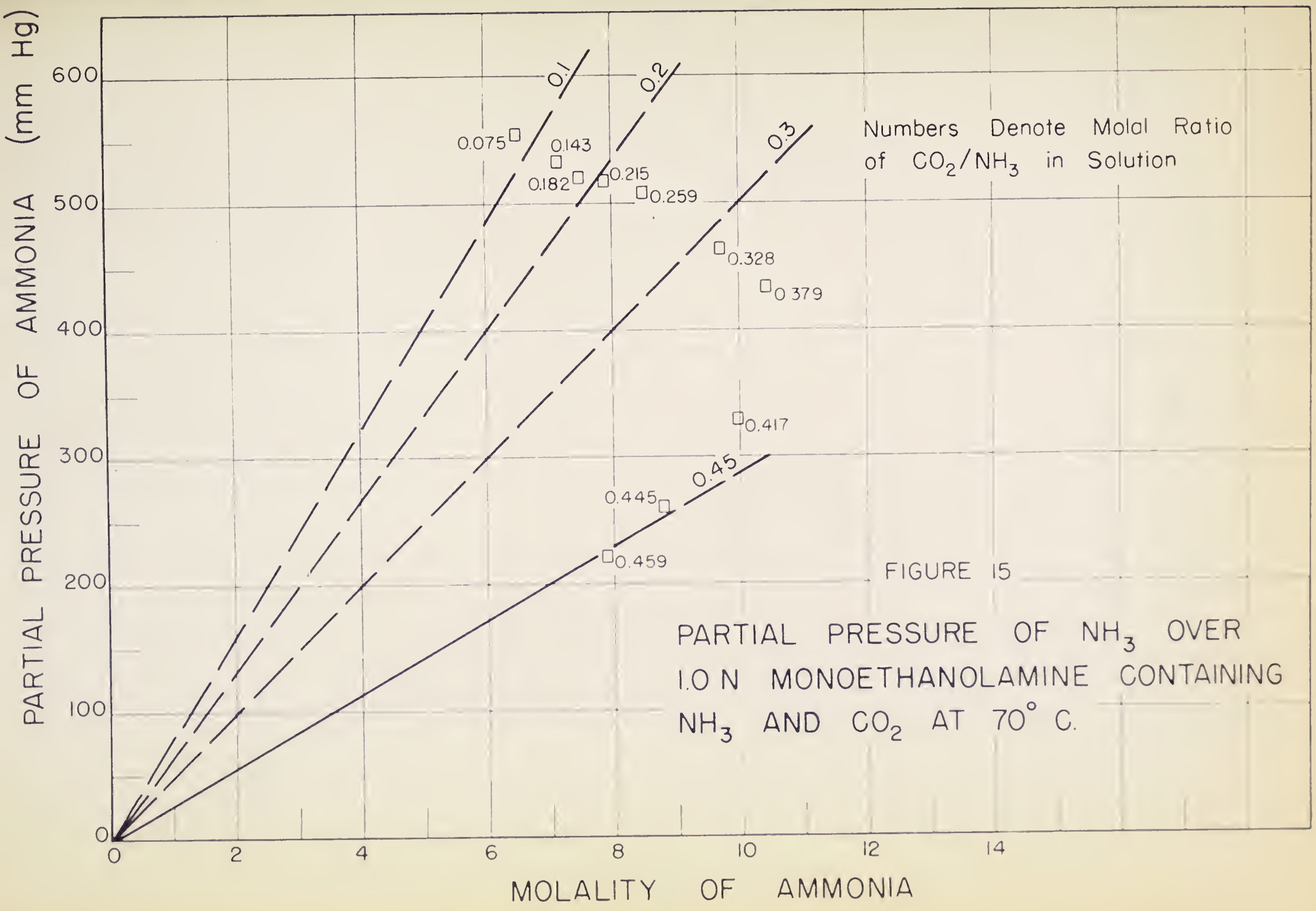


FIGURE 15

PARTIAL PRESSURE OF NH_3 OVER 1.0 N MONOETHANOLAMINE CONTAINING NH_3 AND CO_2 AT 70° C.

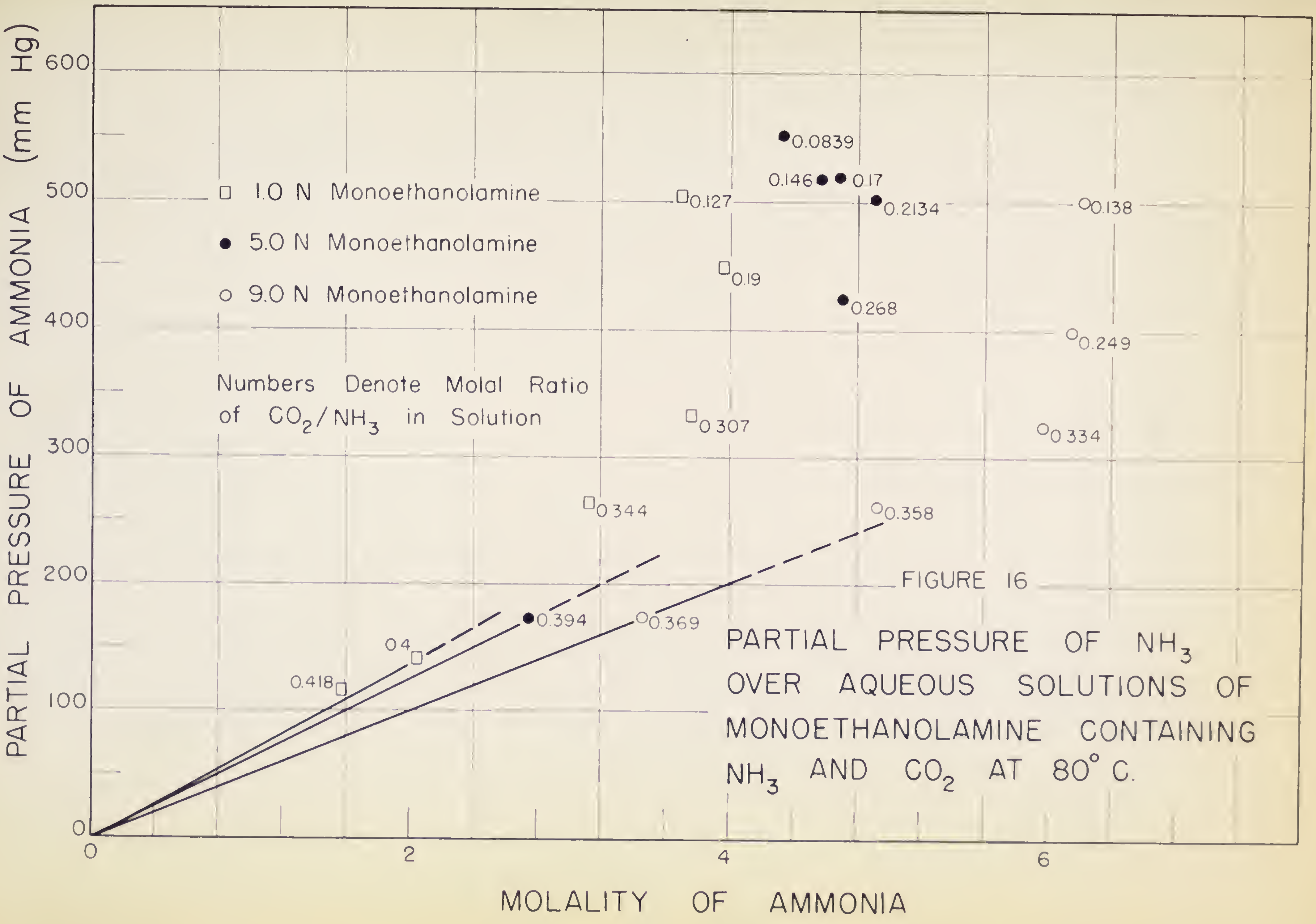


FIGURE 16

PARTIAL PRESSURE OF NH_3 OVER AQUEOUS SOLUTIONS OF MONOETHANOLAMINE CONTAINING NH_3 AND CO_2 AT 80° C.

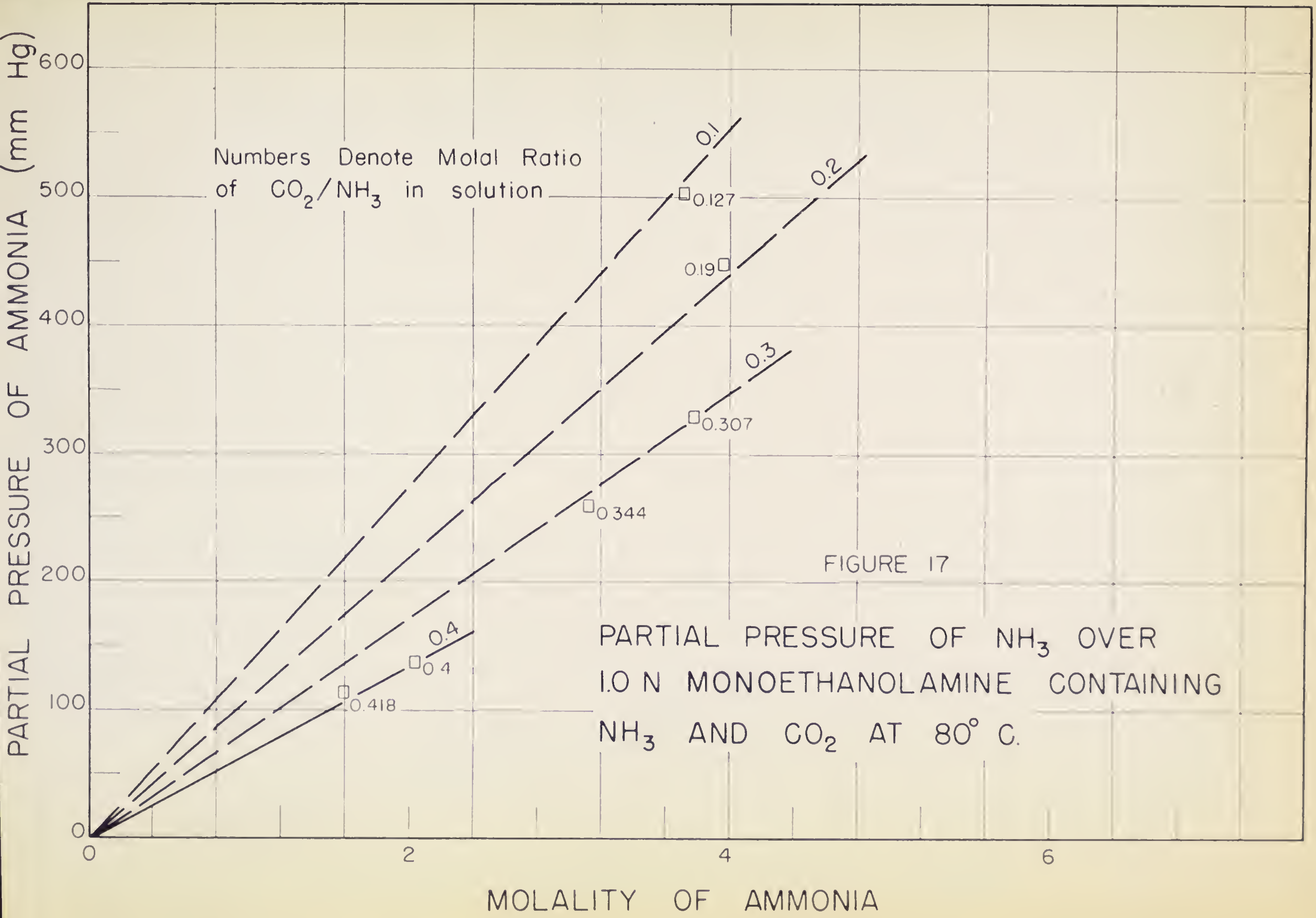


FIGURE 17

PARTIAL PRESSURE OF NH_3 OVER 1.0 N MONOETHANOLAMINE CONTAINING NH_3 AND CO_2 AT 80° C.

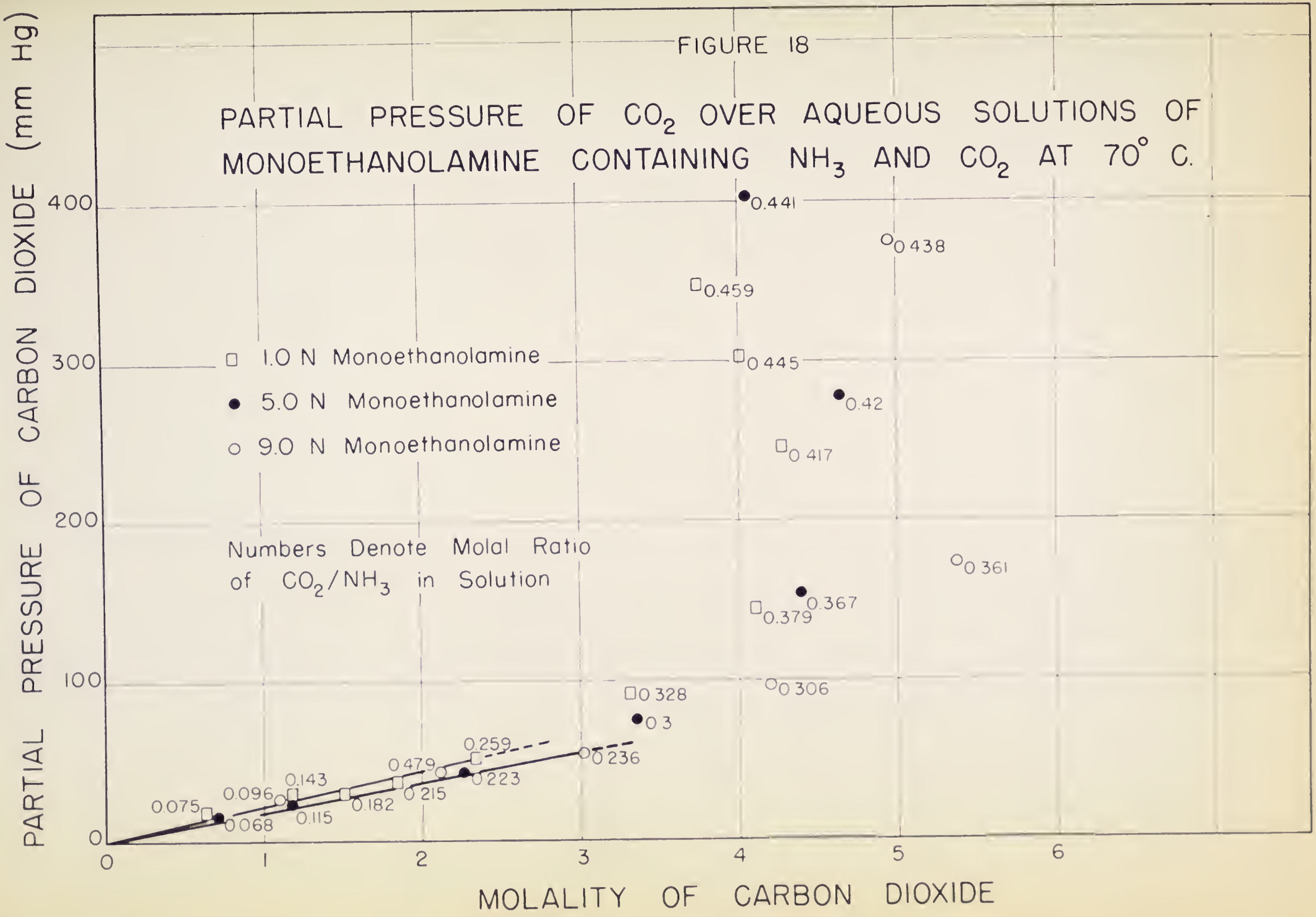
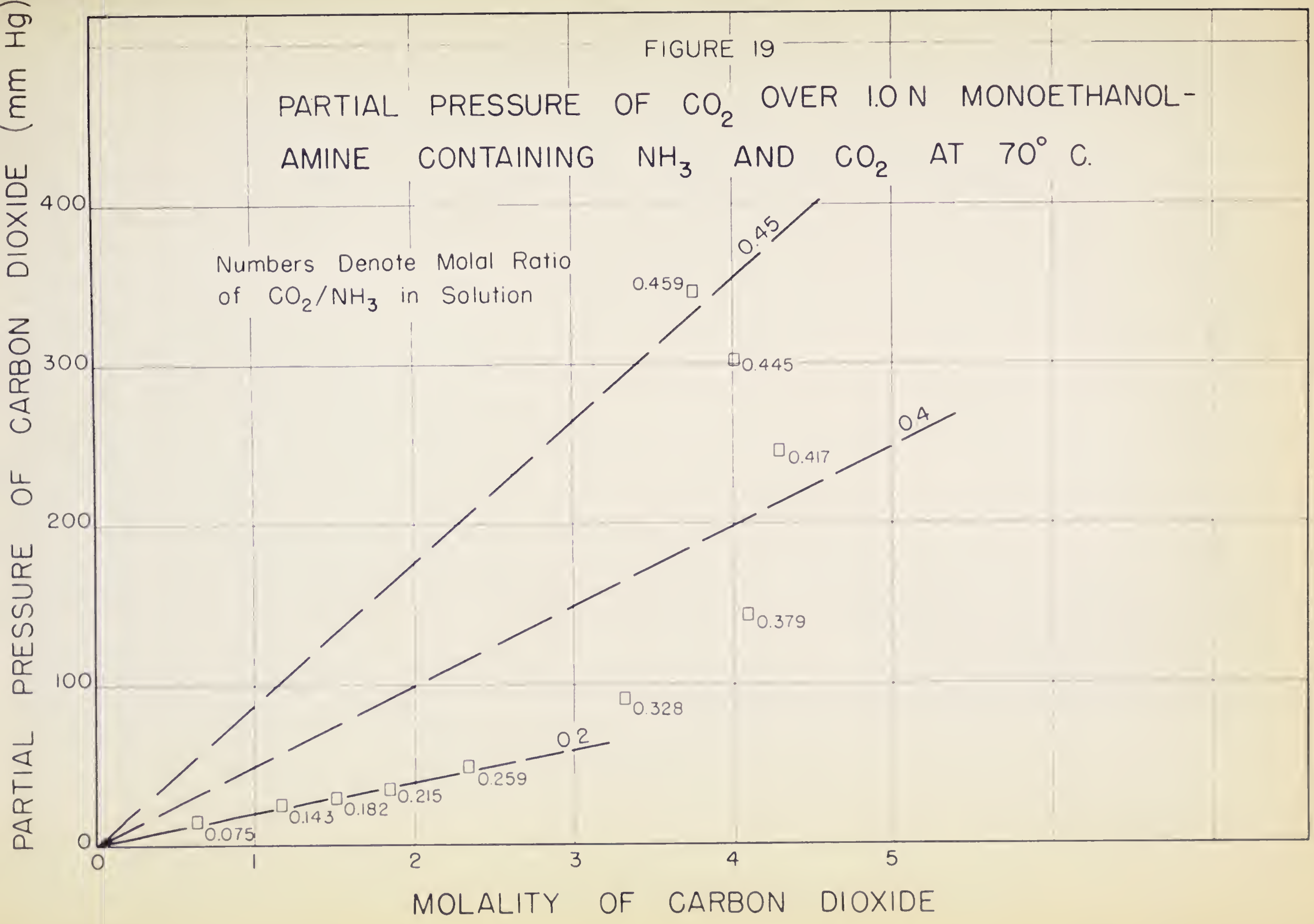


FIGURE 18

PARTIAL PRESSURE OF CO_2 OVER AQUEOUS SOLUTIONS OF MONOETHANOLAMINE CONTAINING NH_3 AND CO_2 AT 70° C.

FIGURE 19

PARTIAL PRESSURE OF CO_2 OVER 1.0 N MONOETHANOLAMINE CONTAINING NH_3 AND CO_2 AT 70° C.



Numbers Denote Molal Ratio of CO_2/NH_3 in Solution

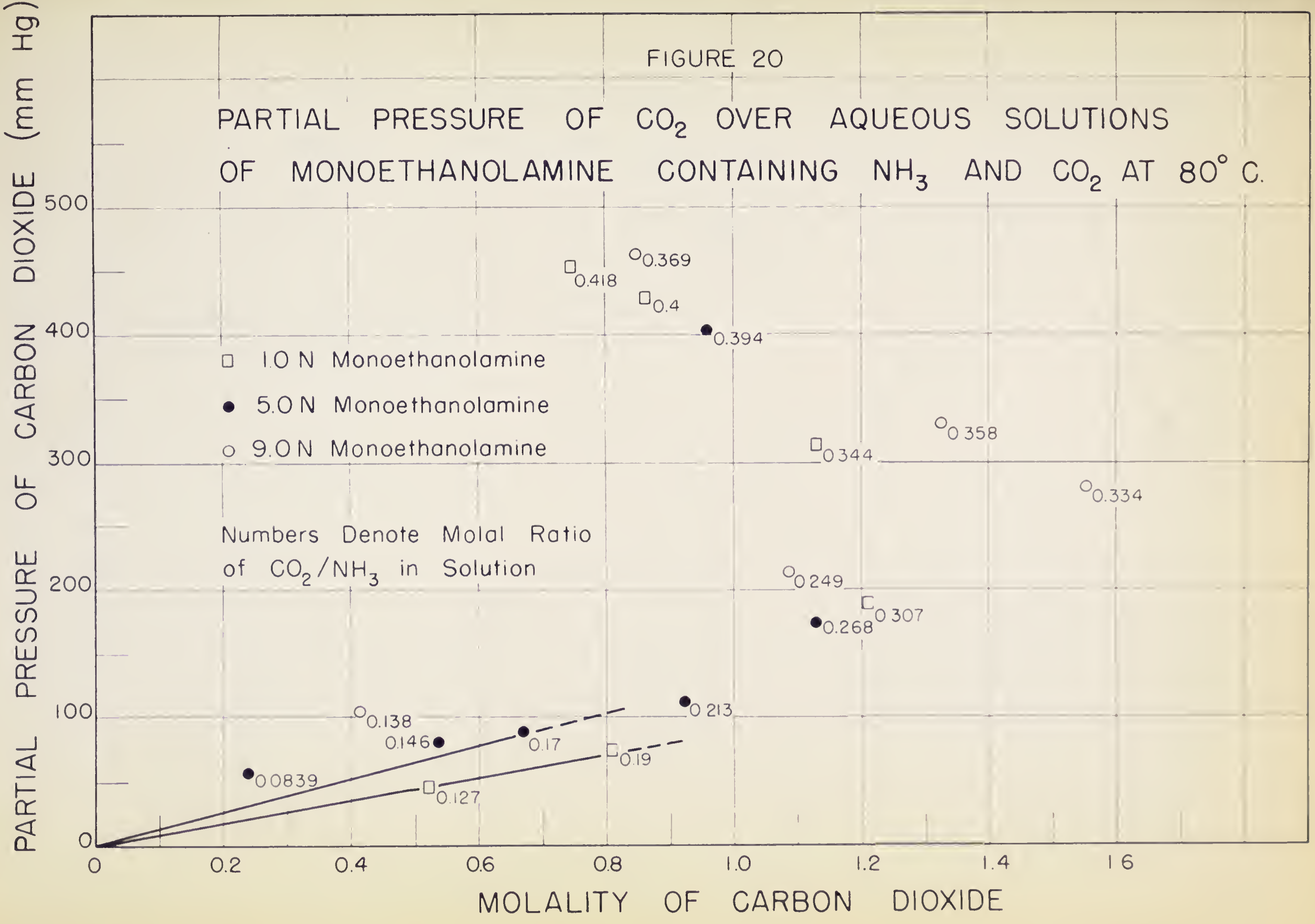


FIGURE 20

PARTIAL PRESSURE OF CO_2 OVER AQUEOUS SOLUTIONS OF MONOETHANOLAMINE CONTAINING NH_3 AND CO_2 AT 80° C.

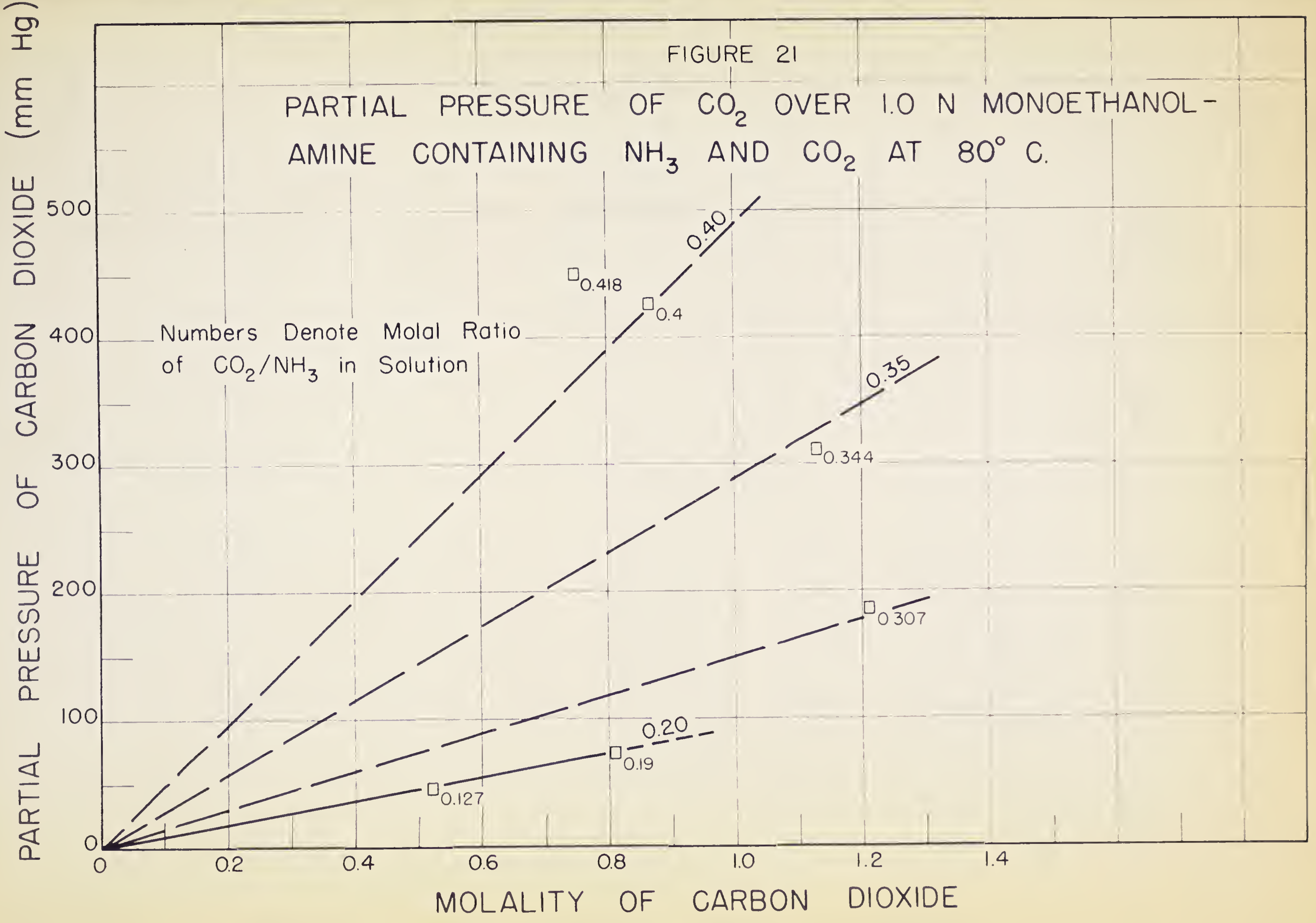


FIGURE 21

PARTIAL PRESSURE OF CO_2 OVER 1.0 N MONOETHANOLAMINE CONTAINING NH_3 AND CO_2 AT 80° C.

VI CONCLUSIONS

Following the discussion of the results, a summary of arising conclusions would have been as follows:

(1) The partition factor of ammonia increases with the increase of the ratio $CO_2:NH_3$ in solution and also with the increase of the normality of the amine solutions. The partition factor of carbon dioxide increases first with rise of the ratio $CO_2:NH_3$ in solution and then decreases for most of the part.

(2) The partial pressure of ammonia decreases but that of carbon dioxide increases with the rise of the ratio $CO_2:NH_3$ in solution and also with the rise of the temperature.

(3) The partial pressures of ammonia and carbon dioxide differ slightly between 1.0 N and 5.0 N monoethanolamine solutions, however there is no significant difference in their partial pressures at higher normalities.

LIST OF REFERENCES

(1) Badger, J. Soc. Chem. Ind., 57, 112, (1938)

(2) Badger and Pexton, J. Soc. Chem. Ind., 57, 106-110, (1938)

(3) Badger and Silver, J. Soc. Chem. Ind., 57, 110-112, (1938)

(4) Bottoms, Ind. Eng. Chem., 23, 501-504 (1931)

(5) Dickson and Jay, Pet. Engineer, 27, Aug C-19 (1955)

(6) Mason and Dodge, Am. Inst. Chem. Engrs., 32, 27, (1936)

(7) Wan, Bronx and Strelzoff, U.S. Patent, 2,785,045

APPENDIX

TABLE I

EXPERIMENTAL DATA

T = 70°C

Run No.	MEA Conc.	Moles CO_2 Added	Moles CO_2 in Vapor	Moles CO_2 in Solution	Moles CO_2 Reacted With MEA	Moles NH_3 Added	Moles NH_3 in Vapor	Moles NH_3 in Solution
1	1N	0.01022	0.00213	0.00809	0.0013	0.01615	0.00136	0.01479
2	1N	0.01047	0.00189	0.00857	0.0013	0.01798	0.00162	0.01635
3	1N	0.01002	0.00095	0.00906	0.0013	0.01986	0.00126	0.01859
4	1N	0.09431	0.00074	0.00869	0.0013	0.02169	0.00221	0.01948
5	1N	0.00756	0.00033	0.00723	0.0013	0.01975	0.00166	0.01809
6	1N	0.00563	0.00023	0.00540	0.0013	0.01819	0.00235	0.01585
7	1N	0.00461	0.00015	0.00446	0.0013	0.01682	0.00211	0.01470
8	1N	0.00334	0.00014	0.00320	0.0013	0.01589	0.00259	0.01330
9	1N	0.00231	0.00010	0.00221	0.0013	0.01504	0.00294	0.01210
10	1N	-	-	-	-	0.01298	0.00285	0.01013
T = 80°C								
11	1N	0.00489	0.00249	0.00240	0.0011	0.00376	0.00064	0.00312
12	1N	0.00489	0.00226	0.00263	0.0011	0.00458	0.00075	0.00383
13	1N	0.00523	0.00211	0.00312	0.0011	0.00765	0.00178	0.00587
14	1N	0.00429	0.00101	0.00328	0.0011	0.00887	0.00178	0.00709
15	1N	0.00294	0.00042	0.00252	0.0011	0.00808	0.00182	0.00626
16	1N	0.00286	0.00034	0.00252	0.0011	0.00951	0.00206	0.00745
17	1N	0.00229	0.00031	0.00198	0.0011	0.01032	0.00337	0.00695
18	1N	-	-	-	-	0.00773	0.00178	0.00595

TABLE I (CONTINUED)

EXPERIMENTAL DATA

T = 70°C

Run No.	MEA Conc.	Moles CO_2 Added	Moles CO_2 in Vapor	Moles CO_2 in Solution	Moles CO_2 Reacted With MEA	Moles NH_3 Added	Moles NH_3 in Vapor	Moles NH_3 in Solution
19	5N	0.01259	0.00194	0.01065	0.00526	0.01340	0.00119	0.01221
20	5N	0.01354	0.00208	0.01146	0.00526	0.01726	0.00248	0.01478
21	5N	0.01169	0.00058	0.01111	0.00526	0.01769	0.00177	0.01592
22	5N	0.01000	0.00033	0.00967	0.00526	0.01702	0.00233	0.01469
23	5N	0.00835	0.00019	0.00816	0.00526	0.01556	0.00248	0.01308
24	5N	0.00751	0.00015	0.00736	0.00526	0.01467	0.00273	0.01194
25	5N	0.00676	0.00013	0.00663	0.00526	0.01400	0.00292	0.01108
26	5N	0.00608	0.00011	0.00597	0.00526	0.01338	0.00310	0.01028
27	5N	0.00544	0.00009	0.00535	0.00526	0.01300	0.00316	0.00984
28	5N	-	-	-	-	0.01026	0.00276	0.00750
				T = 80°C				
29	5N	0.00796	0.00162	0.00634	0.00483	0.00454	0.00071	0.00383
30	5N	0.00736	0.00078	0.00658	0.00483	0.00848	0.00192	0.00656
31	5N	0.00682	0.00054	0.00628	0.00483	0.00923	0.00241	0.00682
32	5N	0.00638	0.00045	0.00593	0.00483	0.00915	0.00264	0.00651
33	5N	0.00616	0.00041	0.00575	0.00483	0.00893	0.00261	0.00632
34	5N	0.00559	0.00026	0.00533	0.00483	0.00856	0.00255	0.00601
35	5N	-	-	-	-	0.00694	0.00242	0.00452

TABLE I (CONTINUED)

EXPERIMENTAL DATA

Run No.	MEA Conc.	Moles CO_2 Added	Moles CO_2 in Vapor	Moles CO_2 in Solution	Moles CO_2 Reacted With MEA	Moles NH_3 Added	Moles NH_3 in Vapor	Moles NH_3 in Solution
				T = 70°C				
36	9N	0.01544	0.00196	0.01348	0.00914	0.01124	0.00132	0.00992
37	9N	0.01480	0.00093	0.01387	0.00914	0.01550	0.00239	0.01311
38	9N	0.01329	0.00048	0.01281	0.00914	0.01451	0.00250	0.01201
39	9N	0.01207	0.00033	0.01174	0.00914	0.01435	0.00335	0.01100
40	9N	0.01118	0.00026	0.01092	0.00914	0.01340	0.00349	0.00991
41	9N	0.01016	0.00015	0.01001	0.00914	0.01219	0.00309	0.00910
42	9N	-	-	-	-	0.00753	0.00267	0.00486
				T = 80°C				
43	9N	0.01177	0.00201	0.00976	0.0086	0.00392	0.00077	0.00315
44	9N	0.01181	0.00161	0.01020	0.0086	0.00577	0.00130	0.00447
45	9N	0.01182	0.00141	0.01041	0.0086	0.00705	0.00163	0.00542
46	9N	0.01111	0.00113	0.00998	0.0086	0.00769	0.00213	0.00556
47	9N	0.00993	0.00055	0.00938	0.0086	0.00822	0.00260	0.00562
48	9N	-	-	-	-	0.00585	0.00285	0.00300
				T = 90°C				
49	5N	0.00600	0.00152	0.00448	0.00426	0.00341	0.00161	0.00180
50	5N	0.00567	0.00126	0.00441	0.00426	0.00385	0.00171	0.00214
51	5N	-	-	-	-	0.00403	0.00233	0.00170

TABLE II

EQUILIBRIUM DATA FOR 1.0 N MONOETHANOLAMINE SOLUTIONS AT ATMOSPHERIC PRESSURE AND 70°C

Run No.	Mole Ratio CO_2/NH_3 in Solution	pp_{NH_3} mm Hg	X_{NH_3} $\frac{\text{Moles Ammonia}}{\text{1000 g. Water}}$	K X_{NH_3} Moles NH_3/litre of gas	pp_{CO_2} mm Hg	X_{CO_2} $\frac{\text{Moles } CO_2}{\text{1000 g. Water}}$	K X_{CO_2} Moles CO_2/litre of gas
1	0.46	223	7.88	775	349	3.78	232
2	0.45	260	8.70	718	302	4.04	286
3	0.42	329	9.91	644	248	4.30	371
4	0.38	433	10.38	513	145	4.09	605
5	0.33	463	9.63	445	92	3.32	775
6	0.26	508	8.44	356	50	2.44	995
7	0.22	515	7.83	325	36	1.85	1083
8	0.14	531	7.09	286	28	1.18	884
9	0.08	555	6.44	249	19	0.64	715
10	0.0	557	5.40	207	-	-	-

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TABLE III

EQUILIBRIUM DATA FOR 1.0 N MONOETHANOLAMINE SOLUTIONS

AT ATMOSPHERIC PRESSURE AND 80°C

Run No.	Mole Ratio CO_2/NH_3 in Solution	PP_{NH_3} mm Hg	X_{NH_3} $\frac{\text{Moles Ammonia}}{\text{1000 g. Water}}$	$K_{X_{NH_3}}$ Moles NH_3/litre of gas	PP_{CO_2} mm Hg	X_{CO_2} $\frac{\text{Moles } CO_2}{\text{1000 g. Water}}$	$K_{X_{CO_2}}$ Moles CO_2/litre of gas
11	0.42	115	1.66	320	451	0.75	36
12	0.40	143	2.04	314	429	0.87	45
13	0.34	263	3.12	261	312	1.13	80
14	0.31	332	3.78	251	188	1.21	142
15	0.23	415	3.80	202	95	0.81	189
16	0.19	449	3.97	195	74	0.81	240
17	0.13	506	3.70	161	46	0.52	251
18	0.0	571	3.17	122	-	-	-

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TABLE IV

EQUILIBRIUM DATA FOR 5.0 N MONOETHANOLAMINE SOLUTIONS

AT ATMOSPHERIC PRESSURE AND 70°C

Run No.	Mole Ratio CO_2/NH_3 in Solution	pp_{NH_3} mm Hg	X_{NH_3} $\frac{\text{Moles Ammonia}}{\text{1000 g. Water}}$	$K_{X_{NH_3}}$ Moles NH_3/litre of gas	pp_{CO_2} mm Hg	X_{CO_2} $\frac{\text{Moles } CO_2}{\text{1000 g. Water}}$	$K_{X_{CO_2}}$ Moles CO_2/litre of gas
19	0.44	246	8.77	763	402	4.05	215
20	0.42	332	10.62	685	278	4.64	358
21	0.37	468	11.44	524	154	4.39	610
22	0.30	528	10.55	528	75	3.36	963
23	0.22	563	9.35	355	43	2.27	1135
24	0.18	570	8.58	322	30	1.70	1201
25	0.12	587	8.60	314	25	1.17	987
26	0.069	599	7.38	264	22	0.69	678
27	0.0095	599	7.07	253	17	0.25	326
28	0.0	599	5.40	193	-	-	-

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TABLE V

EQUILIBRIUM DATA FOR 5.0 N MONOETHANOLAMINE SOLUTIONS

AT ATMOSPHERIC PRESSURE AND 80°C

Run No.	Mole Ratio CO_2/NH_3 in Solution	pp_{NH_3} mm Hg	X_{NH_3} $\frac{\text{Moles Ammonia}}{\text{1000 g. Water}}$	$K_{X_{NH_3}}$ $\frac{}{\text{Moles } NH_3\text{/litre of gas}}$	pp_{CO_2} mm Hg	X_{CO_2} $\frac{\text{Moles } CO_2}{\text{1000 g. Water}}$	$K_{X_{CO_2}}$ $\frac{}{\text{Moles } CO_2\text{/litre of gas}}$
29	0.39	175	2.76	345	505	0.96	52
30	0.27	425	4.71	244	173	1.14	145
31	0.21	502	4.90	215	112	0.92	181
32	0.17	521	4.68	198	88	0.67	169
33	0.15	524	4.54	191	82	0.54	145
34	0.084	551	4.32	173	56	0.24	93
35	0.0	601	3.25	120	-	-	-

TABLE VI

EQUILIBRIUM DATA FOR 9.0 N MONOETHANOLAMINE SOLUTIONS AT ATMOSPHERIC PRESSURE AND 70°C

Run No.	Mole Ratio CO_2/NH_3 in Solution	pp_{NH_3} mm Hg	X_{NH_3} $\frac{\text{Moles Ammonia}}{\text{1000 g. Water}}$	K $\frac{X_{NH_3}}{\text{Moles } NH_3\text{/litre of gas}}$	pp_{CO_2} mm Hg	X_{CO_2} $\frac{\text{Moles } CO_2}{\text{1000 g. Water}}$	K $\frac{X_{CO_2}}{\text{Moles } CO_2\text{/litre of gas}}$
36	0.44	254	10.94	922	577	4.95	281
37	0.36	449	14.46	690	174	5.38	662
38	0.31	507	13.25	559	97	4.21	934
39	0.24	550	12.14	473	54	3.02	1194
40	0.18	556	10.94	421	42	2.12	1086
41	0.096	569	10.04	578	28	1.12	868
42	0.0	579	5.36	198	-	-	-

TABLE VII

EQUILIBRIUM DATA FOR 9.0 N MONOETHANOLAMINE SOLUTIONS

AT ATMOSPHERIC PRESSURE AND 80°C

Run No.	Mole Ratio CO_2/NH_3 in Solution	pp_{NH_3} mm Hg	X_{NH_3} $\frac{\text{Moles Ammonia}}{\text{1000 g. Water}}$	$K_{X_{NH_3}}$ Moles NH_3/litre of gas	pp_{CO_2} mm Hg	X_{CO_2} $\frac{\text{Moles } CO_2}{\text{1000 g. Water}}$	$K_{X_{CO_2}}$ Moles CO_2/litre of gas
43	0.37	178	3.48	430	464	0.84	53
44	0.36	264	4.94	411	329	1.32	89
45	0.33	325	5.98	405	280	1.56	125
46	0.25	400	6.14	338	211	1.01	113
47	0.14	502	6.21	272	107	0.42	85
48	0.0	217	3.32	119	-	-	-

TABLE VIII

EQUILIBRIUM DATA FOR 5.0 N MONOETHANOLAMINE SOLUTIONS AT ATMOSPHERIC PRESSURE AND 90°C

Run No.	Mole Ratio CO_2/NH_3 in Solution	pp_{NH_3} mm Hg	X_{NH_3} $\frac{\text{Moles Ammonia}}{\text{1000 g. Water}}$	$K_{X_{NH_3}}$ $\frac{}{\text{Moles } NH_3\text{/litre of gas}}$	pp_{CO_2} mm Hg	X_{CO_2} $\frac{\text{Moles } CO_2}{\text{1000 g. Water}}$	$K_{X_{CO_2}}$ $\frac{}{\text{Moles } CO_2\text{/litre of gas}}$
49	0.12	229	1.29	128	216	0.16	16
50	0.070	294	1.54	119	216	0.11	11
51	0.0	446	1.22	62	-	-	-

TABLE IX

EQUILIBRIUM DATA FOR MONOETHANOLAMINE SOLUTIONS CONTAINING CARBON DIOXIDE

Temperature °C	Normality of Amine	Total Pressure mm Hg	Liquid Conc. Moles CO_2 per Mole Amine
70.0	1.0	703	0.65
70.0	5.0	707	0.53
70.0	9.0	704	0.51
80.0	1.0	699	0.55
80.0	5.0	699	0.48
80.0	9.0	700	0.42
90.0	5.0	704	0.43

TABLE X

PARTIAL PRESSURES OF WATER VAPOR OVER AQUEOUS SOLUTIONS OF MONOETHANOLAMINE

Run No.	Experimental Value mm Hg	Calculated Value (using Raoult's law) mm Hg	Total Pressure mm Hg
1	130	190	702
2	136	187	698
3	130	183	707
4	122	183	699
5	149	186	704
6	146	193	704
7	156	196	708
8	142	200	701
9	128	202	702
10	141	202	699
11	143	334	709
12	140	331	712
13	131	324	706
14	178	320	699
15	188	292	698
16	180	321	703
17	158	324	709
18	166	330	702
19	53	171	701
20	92	166	702
21	82	165	703
22	98	169	701
23	104	175	710
24	102	183	702
25	93	179	706
26	80	183	702
27	89	176	704
28	107	189	706
29	128	297	708
30	108	287	706

TABLE X (Continued)

PARTIAL PRESSURES OF WATER VAPOR OVER AQUEOUS SOLUTIONS OF MONOETHANOLAMINE

Run No.	Experimental Value mm Hg	Calculated Value (using Raoult's law) mm Hg	Total Pressure mm Hg
31	93	288	708
32	97	290	706
33	101	291	707
34	97	293	704
35	106	328	706
36	71	142	702
37	84	136	707
38	100	139	706
39	91	143	705
40	105	147	703
41	109	150	706
42	127	159	706
43	69	220	710
44	115	241	709
45	96	238	701
46	87	239	698
47	90	240	699
48	87	250	704
49	252	455	707
50	199	454	708
51	256	510	702

TABLE XI

COMPARISON OF EXPERIMENTAL RESULTS WITH THOSE OF MASON AND DODGE FOR AQUEOUS SOLUTIONS OF MONOETHANOLAMINE AT 70°C

Normality of Amine	CO_2 Pressure mm Hg	Liquid Conc., Moles CO_2 per Mole Amine (experimental)	Liquid Conc., Moles CO_2 per Mole Amine (M and D)
1.0	585	0.65	0.63
5.0	596	0.53	0.52
9.0	580	0.51	0.48

TABLE XII

SPECIFIC GRAVITY OF AQUEOUS SOLUTIONS OF MONOETHANOLAMINE AT 20/20°

% by Wt.	Sp. Gravity
0	1.00
10	1.005
20	1.011
30	1.016
40	1.022
50	1.027
60	1.030
70	1.032
80	1.030
100	1.022

SAMPLE CALCULATIONS

System: Carbon dioxide-Ammonia in 1.0 N monoethanolamine

Equilibrium Condition: $T = 70^{o}C$

$P = 699$ mm Hg

(1) Addition of CO_2 to equilibrium cell:

$P = 13.52$ Psia

$T = 75.2^{o}F = 535.2^{o}R$

$V = 250.2$ c.c.

$$n = \frac{pv}{RT} = \frac{13.52 \times 250.2}{670 \times 535.2}$$

$$= 0.009430 \text{ gm. moles}$$

(2) Addition of NH_3 to equilibrium cell:

$P = 13.52$ Psia

$T = 75.2^{o}F = 535.2^{o}R$

$V = 575.6$

$$n = \frac{pv}{RT} = \frac{13.52 \times 575.6}{670 \times 535.2}$$

$$= 0.0217 \text{ gm. moles}$$

(3) Total moles of gas phase:

$P = 107.5$ mm Hg

$T = 110.8^{o}F = 570.8^{o}R$

Volume of flask = 657.135 c.c.

$$n = \frac{pv}{RT} = \frac{107.5 \times 14.7 \times 657.135}{670 \times 760 \times 570.8}$$

$$= 0.00357 \text{ gm. moles}$$

(4) Partial Pressures of NH_3 and CO_2:

$y_{NH_3} = 0.62$

$pp_{NH_3} = Py_{NH_3} = 699.0 \times 0.62$

$= 433$ mm Hg

$y_{CO_2} = 0.21$

$pp_{CO_2} = Py_{CO_2} = 699.0 \times 0.21$

$= 145$ mm Hg

$pp_{H_2O} = 699.0 - 433 - 145$

$= 121$ mm Hg

(5) Ratio CO_2/NH_3 in solution:

Total CO_2 introduced = 0.009430 gm. moles

CO_2 in vapor phase = 0.00074 gm. moles

CO_2 reacted with monoethanolamine = 0.0013 gm. moles

CO_2 in solution (on water basis)

= 0.00943 - 0.00074 - 0.0013

= 0.00739 gm. moles

Total NH_3 introduced = 0.02170 gm. moles

NH_3 in vapor phase = 0.002210 gm. moles

NH_3 in solution = 0.02170 - 0.002210

= 0.0195 gm. moles

Ratio CO_2/NH_3 in solution $= \frac{0.00739}{0.0195}$

= 0.38

(6) 1000 gm. of 1N MEA Contain 938.91 gm. H_2O

2 gm. of 1N MEA Contain $\frac{938.91 \times 2}{1000}$

$= 1.877$ gm. H_2O

$= 1.877$ c.c. H_2O

(7) Molality of NH_3 and CO_2:

$$x_{NH_3} = \frac{\text{Moles of } NH_3 \text{ in water}}{\text{c.c. of water in solution}} \times 10^3$$

$$= \frac{0.0195}{1.877} \times 10^3$$

$$= 10.38 \text{ moles/litre } H_2O$$

$$x_{CO_2} = \frac{\text{Moles of } CO_2 \text{ in water}}{\text{c.c. of water in solution}} \times 10^3$$

$$= \frac{0.00739}{1.877} \times 10^3$$

$$= 4.09 \text{ moles/litre } H_2O$$

(8) Partition Factor of NH_3 and CO_2:

$$K_{NH_3} = \frac{X_{NH_3}}{\text{Moles of } NH_3\text{/litre gas}}$$

$$= \frac{X_{NH_3}}{\frac{p}{760} \times \frac{1}{22.42} \times \frac{273.1}{T}}$$

$$= \frac{10.38}{\frac{432.68}{760} \times \frac{1}{22.42} \times \frac{273.1}{343.1}}$$

$$= 513$$

$$K_{CO_2} = \frac{X_{CO_2}}{\text{Moles } CO_2\text{/litre gas}}$$

$$= \frac{X_{CO_2}}{\frac{p}{760} \times \frac{1}{22.42} \times \frac{273.1}{T}}$$

$$= \frac{4.09}{\frac{144.62}{760} \times \frac{1}{22.42} \times \frac{273.1}{343.1}}$$

$$= 605$$

(9) Partial Pressure of H_2O from Raoult's Law:

Total Moles in Solution:

$CO_2 = 0.00869$

$NH_3 = 0.01948$

$MEA = 0.00200$

$H_2O = \underline{0.10427}$

0.13444

$$x_{H_2O} = \frac{0.10427}{0.13444} = 0.78$$

$$PP_{H_2O} = XP_{vp} = 0.78 \times 233.7 = 183$$

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